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EVALUATION OF POLLUTION CONTROL IN FOSSIL FUEL
CONVERSION PROCESSES

GASIFICATION, SECTION I, SYNTHANE PROCESS

Esso Research and Engineering Company

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The report gives results of a review of the U. S. Bureau of Mines' Synthane Coal Gasification Process, from the standpoint of its potential for affecting the environment. Where possible, it estimates the quantities of solid, liquid, and gaseous effluents, as well as the thermal efficiency of the process. It proposes a number of possible process modifications or alternates, and points out new technology needs.

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GASIFICATION; SECTION I: SYNTHANE PROCESS

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SUMMARY

The Bureau of Mines Synthane Coal Gasification Process has been reviewed from the standpoint of its potential for affecting the environment. The quantities of solid, liquid and gaseous effluents have been estimated, where possible, as well as the thermal efficiency of the process. A number of possible process modifications or alternatives have been proposed and new technology needs have been pointed out.

TABLE OF CONVERSION UNITS

<u>To Convert From</u>	<u>To</u>	<u>Multiply By</u>
Btu	Calories, kg	0.25198
Btu/pound	Calories, kg/kilogram	0.55552
Cubic feet/day	Cubic meters/day	0.028317
Feet	Meters	0.30480
Gallons/minute	Cubic meters/minute	0.0037854
Inches	Centimeters	2.5400
Pounds	Kilograms	0.45359
Pounds/Btu	Kilograms/calorie,kg	1.8001
Pounds/hour	Kilograms/hour	0.45359
Pounds/square inch	Kilograms/square centimeter	0.070307
Tons	Metric tons	0.90719
Tons/day	Metric tons/day	0.90719

INTRODUCTION

Along with improved control of air and water pollution, the country is faced with urgent needs for energy sources. To improve the energy situation, intensive efforts are under way to upgrade coal, the most plentiful domestic fuel, to liquid and gaseous fuels which give less pollution. Other processes are intended to convert liquid fuels to gas. A few of the coal gasification processes are already commercially proven, and several others are being developed in large pilot plants. These programs are extensive and will cost millions of dollars, but this is warranted by the projected high cost for commercial gasification plants and the wide application expected in order to meet national needs. Coal conversion is faced with potential pollution problems that are common to coal-burning electric utility power plants in addition to pollution problems peculiar to the conversion process. It is thus important to examine the alternate conversion processes from the standpoint of pollution and thermal efficiencies and these should be compared with direct coal utilization when applicable. This type of examination is needed well before plans are initiated for commercial applications. Therefore, the Environmental Protection Agency arranged for such a study to be made by Exxon (formerly Esso) Research & Engineering Company under contract EPA-68-02-0629, using all available non-proprietary information.

Phase I of the contract involved the collection and evaluation of published information concerning trace elements in coal, crude oil and shale. This information is contained in the report, "Potential Pollutants in Fossil Fuels", by E. M. Magee, H. J. Hall and G. M. Varga, Jr., EPA-R2-73-249, June 1973 (NTIS PB #225,039). Phases II and III were concerned with the collection of published information on fossil fuel conversion/treatment processes and the description of selected processes. These selected processes were evaluated for their ability to produce clean fuels and for their possibilities for environmental pollution.

The present study, Phase IV of the contract, involves preliminary design work to assure the processes are free from pollution where pollution abatement techniques are available, to determine the overall efficiency of the processes and to point out areas where present technology and information are not available to assure that the processes are non-polluting.

All significant input streams to the processes must be defined, as well as all effluents and their compositions. This requires complete mass and energy balances to define all gas, liquid, and solid streams. With this information, facilities for control of pollution can be examined and modified as required to meet Environmental Protection Agency objectives. Thermal efficiency is also calculated, since it indicates the amount of waste heat that must be rejected to ambient air and water and is related to the total pollution necessary to produce a given quantity of clean fuel.

Alternatively, it is a way of estimating the amount of raw fuel resources that is consumed in making the relatively pollution-free fuel. At this time of energy shortage this is an important consideration. Suggestions are included concerning technology gaps that exist for techniques to control pollution or conserve energy. Maximum use was made of the literature and information available from developers. Visits with some of the developers were made, when it appeared warranted, to develop and update published information. Not included in this study are such areas as cost, economics, operability, etc. Coal mining and general offsite facilities are not within the scope of this study.

Considerable assistance was received in making this study, and we wish to acknowledge the help and information furnished by EPA, the Bureau of Mines, and the Lummus Company, as well as that furnished by many specialists in Exxon Research and Engineering Company.

1. PROCESS DESCRIPTION AND EFFLUENTS - GENERAL

The Synthane Process being developed by the Bureau of Mines is an intrinsically high efficiency fluidized bed coal gasification system operating at commercial pipeline pressure and designed to produce high-Btu content product gas. Gasification is accomplished in the presence of steam/oxygen, whereby heat required for the gasification reactions is supplied by the reaction of oxygen with a portion of the coal. High pressure favors methane yield, minimizes gasifier volume, reduces oxygen requirement and reduces product gas compression. A good fluidized bed operation insures the homogeneous reaction system required to avoid damage by locally high oxygen concentrations.

Development work was started in 1961 by the Bureau of Mines on methods of pretreating caking coals in a fluidized bed. It was found possible to pretreat any caking coal by the proper combination of oxygen content of the fluidizing gas, temperature, and residence time (1,2,3). Earliest gasification tests with a two-bed fluid system incorporating gas, tar, and char recycle (4) led to the development of a single vessel system wherein the operations of coal pretreatment, carbonization, and gasification were combined (5).

An engineering evaluation of the Synthane Process, which by this time incorporated Bureau of Mines methanation developments (6,7), was prepared by The M.W. Kellogg Company in 1970 (8). Notwithstanding the substantial extension of high-pressure technology required to commercialize the process, there was found sufficient incentive in the economies projected in terms of overall simplicity, high gasifier methane yield, and small reaction volumes to proceed with design of a prototype large pilot plant. The prototype pilot plant was designed by The Lummus Company (9), and is now being constructed. It is expected to be operational in 1974.

The process basis for our evaluation is that employed by the Bureau of Mines in its economic evaluation of Synthane Gasification (10) in 1971. A block flow diagram of the process and auxiliary facilities is shown in Figure 1. This design feeds 14,250 tpd of a Pittsburgh seam coal containing 2.5% moisture, 7.4% ash, and 1.6% sulfur to the gasifiers. 250MM scfd of product gas is produced, with a HHV of 927 Btu/scf.

The design basis for the economic evaluation was based on laboratory investigation in a forty-atmosphere fluid-bed gasifier (11). Although serving adequately to define the major processing hardware and energy requirements, so that economic comparisons might be made with other gasification processes in a similar stage of development, the basis did not detail disposition of effluent streams which might require special

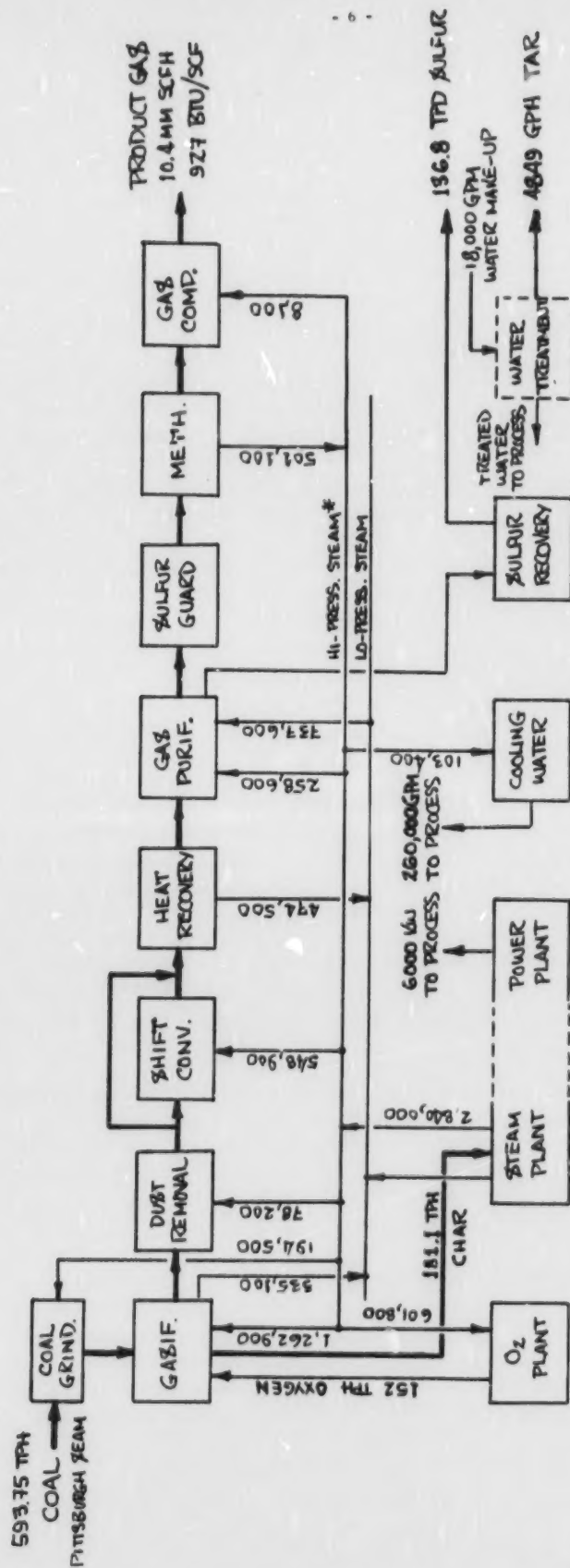


FIGURE 1. SYNTHANE COAL GASIFICATION - 250 million SCFD High - BTU Gas
(Bureau of Mines Report No. 72-9A, October, 1971)

*Steam Rates in Lb/Hr

C.D.V.

processing to minify environmental impact. In fact, until process stream compositions are more precisely determined for specific feed coals, the nature of such effluent streams, and the degree of processing required, may only be inferred. Second after achievement of primary gasification targets, the definition of a process's pollution potential is a major justification for the construction and operation of a large pilot plant.

The pollution potential has not been completely defined in the context of U.S. standards even for those gasification processes which have already been commercialized elsewhere. Standards have changed radically in recent years, and new standards continue to be promulgated by governing agencies at a high rate. Coal compositions, including sulfur and trace element contents, vary widely (12), even within particular regions or mines. Stream compositions from a particular process are generally sensitive to coal composition as well as to specific operating conditions.

On the other hand, gross estimates of the pollution potential may be inferred on the basis of prior art and experience with processes which treat coal or petroleum in analogous manner. There is no direct commercial coal gasification prior art for the extreme pressure at which the Synthane gasifier will operate. Synthane gasification approaches conditions which obtain in the commercialized Lurgi system, but the Lurgi gasifiers are "fixed-bed" devices operating at less than half the pressure of the Synthane fluid-bed units. The present Lurgi gasifier is more restrictive with respect to feed coal physical properties than should be the case with the Synthane system, which incorporates integral pretreatment. But a direct comparison of the pollution potential of the two systems must await considerable further development.

2. EFFLUENTS TO AIR - MAIN GASIFICATION STREAM

All effluents to the air are shown in Figure 2 and Table 1. These effluents are based on the Bureau of Mines design (10), and are to some degree inferred by analogy with prior art. Because of the large number of options open to Synthane development at this stage relative to established processes, there is every probability that substantial modification and/or improvement may be expected.

2.1 Coal Preparation and Storage

Common to all fuel coal usage, and particularly to coal gasification processes, are the operations of coal mining, which may include coal laundering, drying, and screening, coal transport, and storage. This study does not include energy and/or pollution considerations relative to these operations.

On-site coal storage will be required for all gasification plants to provide back-up for continuous gasification operations. For thirty days storage, there might be four piles, each about 200 feet wide, 20 feet high, and 1000 feet long. Containment of air-borne dusts is generally the only air pollution control required for transport and storage operations, although odor may be a problem in some instances. Covered or enclosed conveyances with dust removal equipment may be necessary, but precautions must be taken against fire or explosion. Circulating gas streams which may be used to inert or blanket a particular operation or which may issue from drying operations will generally require treatment to limit particulate content before discharge to the atmosphere (14). Careful management and planning will minimize dusting and wind loss and the hazard of combustion in storage facilities.

The feed coal employed in this design has low inherent moisture content, such that a special coal drying step is not provided. It may be possible to operate the system without such a facility with coal from particular seams, but this indicates enclosed on-site storage. Coal of the type and size range (-3/4 inch) indicated to be held in stockpiles in this design might be expected to acquire and retain 6-8 weight per cent surface moisture on exposure to rain.

Should drying be required, however, the options available are numerous, both with respect to procedures and to the fuel or heat source that may be employed. Comments relating to coal drying in connection with the Koppers Process (14) are pertinent. Ideally, no additional fuel would be combusted specifically for coal drying purposes, but rather hot gas, as, for example, flue gas from the utility boiler, would be used. Overall energy debits would be minor in such case. The gas

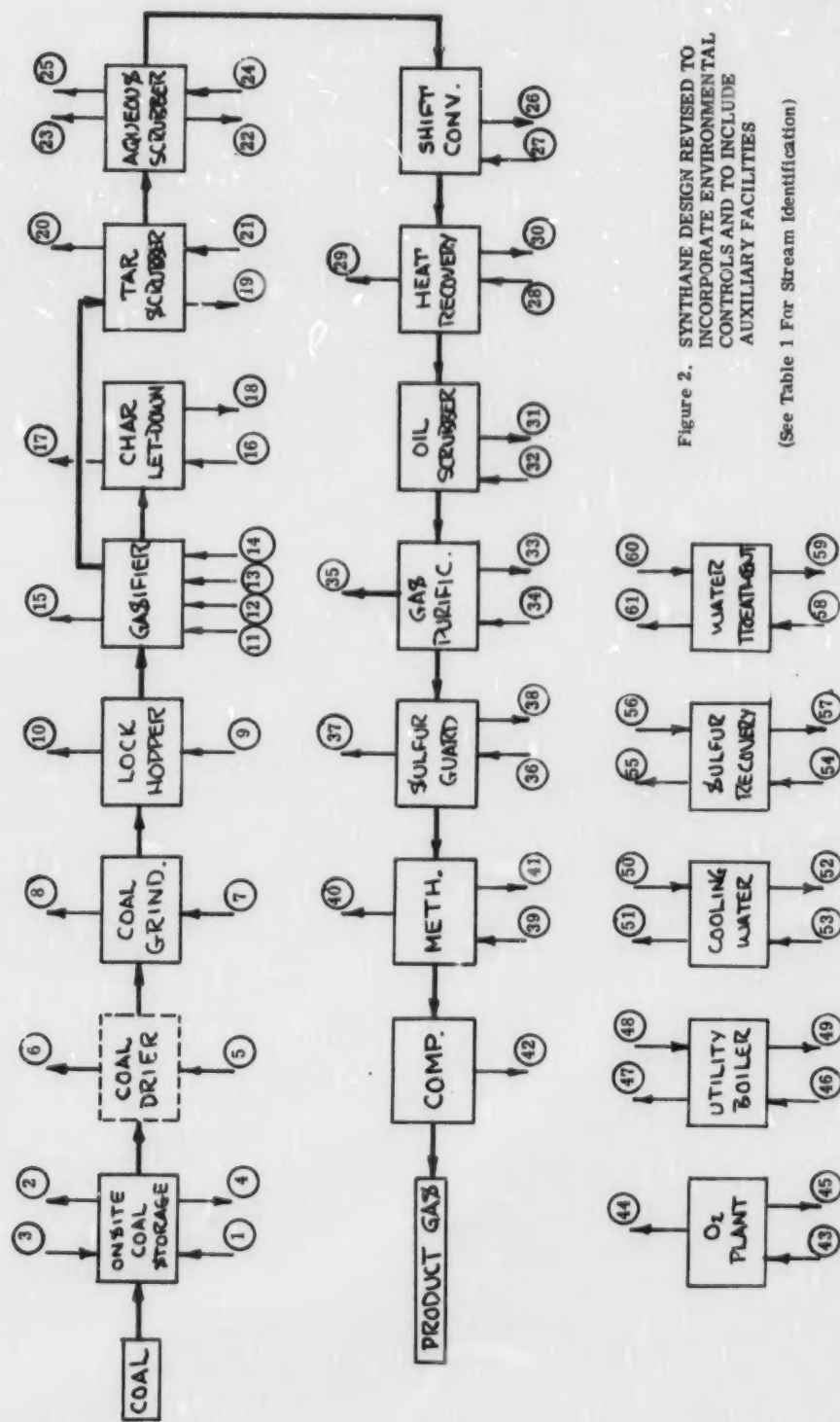


Figure 2. SYNTHANE DESIGN REVISED TO INCORPORATE ENVIRONMENTAL CONTROLS AND TO INCLUDE AUXILIARY FACILITIES
(See Table 1 For Stream Identification)

C.D.V.

TABLE 1

STREAM IDENTIFICATIONS FOR REVISED SYNTHANE PROCESS

(Stream Numbers Refer to Figure 2. See Text for Details)

COAL PREPARATION

• Coal Storage

1. Influence of weather (wind, temperature) on 20-25 acre on-site coal storage piles.
2. Dusting and wind losses; possible odor.
3. Precipitation on 20-25 acre storage area.
4. Storm run-off estimated at 5000 gpm contains particulates and may be sulfidic. Directed to "oily water" retention ponds along with run-off from processing areas for subsequent addition to waste water treatment system.

• Coal Drying

5. No drying facility provided in base case. Assume utility boiler flue-gas stream used for drying coal if required.
6. Assume 6% moisture retained on coal stored openly is removed, equivalent to 72,000 lb/hr water evaporated. Vent gas stream directed to limestone scrubbing facility for particulate removal and desulfurization.

• Coal Grinding

7. 53 MM cfd air intake to milling circuit. Nitrogen from oxygen plant may be substituted in any proportion to reduce fire hazard. Nitrogen from the oxygen plant may be used to blanket storage hoppers or transport facilities. High-pressure steam may be used as transport medium for ground coal in pipe ducts.
8. Outflow stream includes up to 60 tpd coal fines (removed at bag filters and returned to coal feed bins) and up to 20,000 lb/hr water vapor.

GASIFICATION

• Coal Feed Lock Hoppers

9. Treated CO₂ separated at sulfur recovery unit used as make-up to recycled gas pressurization system, amounting to 30-50 MM cfd.
10. No effluent to atmosphere excepting leakage at gas storage facilities; leakage into process of 30-50 MM cfd with coal feed.

• Gasifiers

11. 1,187,500 lb/hr coal feed (see text for analysis).
12. 304,000 lb/hr oxygen feed.
13. 1,169,700 lb/hr high-pressure steam feed.
14. Boiler feed water to cooling jacket, 675 gpm.
15. Low-pressure steam from cooling jacket, 335,100 lb/hr.
16. 200 gpm boiler feed water to "dry char" cooler.
17. 100,000 lb/hr high pressure steam directed to shift converters. 3000-6000 lb/hr vented steam treated to remove particulates if discharged to atmosphere; may be used to transport char to boiler or may be directed to water treatment facilities.
18. 4350 tpd char, assumed dry. Ducted to utility boiler using steam as transport medium.

• Char Let-Down

DUST REMOVAL

• Tar Scrubber

19. Up to 3350 gph heavy tar recycled to gasifier, processed for sale, or directed to utility boiler.
20. Up to 365,000 lb/hr high-pressure steam generated in external tar-cooling circuit.
21. 730 gpm boiler feed water to tar cooler.

• Aqueous Scrubber

22. 1,110,000 lb/hr aqueous scrubber effluent, directed to waste water treatment; depending on operating conditions, an additional 1500 gph of tar and 6-7 tpd of ammonia may be separated from raw gas, in addition to phenols and oils.
23. No discharge to atmosphere; 20-30,000 acfm raw gas evolved on depressurization of scrubber effluent recompressed into main gasification stream ahead of gas purification.
24. 600 gpm boiler feed water to scrubber cooling circuit.
25. 300,000 lb/hr low-pressure steam generated in cooling circuit.

TABLE 1 (Cont'd)

STREAM IDENTIFICATIONS FOR REVISED SYNTHANE PROCESS

(Stream Numbers Refer to Figure 2. See Text for Details)

<u>SHIFT CONVERSION</u>	26. Spent catalyst (3-year life normal).
	27. 548,900 lb/hr high-pressure superheated steam.
<u>HEAT RECOVERY</u>	28. 950 gpm boiler feed water to waste heat boiler.
	29. 474,500 lb/hr low-pressure steam.
	30. 395,000 lb/hr condensate directed to waste water treatment. Gases which separate on decompression reinjected into main gasification stream via routing for stream 23.
<u>OIL SCRUBBER</u>	31. Up to 1000 gph naphtha in scrubbing oil stream, depending on operation of upstream scrubbers. This system integrated with oil recovered from aqueous scrubbing effluents (used as scrubbing medium). Up to 25,000 lb/hr low-pressure steam required for distillation of naphtha.
	32. 18,000 lb/hr high-pressure resaturation steam.
<u>GAS PURIFICATION</u>	33. 19,000 lb/hr condensate from after-cooler directed to waste water treatment. Spent Benfield solution and/or blowdown (life not estimated) requires special treatment. Gases which separate from condensates or blow-down on depressurization directed to utility boiler.
	34. 737,600 lb/hr low-pressure steam into regenerators.
	35. No discharge to atmosphere. 270 MM cfd acid gas stream directed to sulfur recovery. Up to 1.0 MM cfd product gas lost into acid gas stream.
<u>SULFUR GUARD</u>	36. Regeneration gas or steam; inerting gas required on change-out of bed material.
	37. Discharges to atmosphere may include clean regeneration or inerting gases. Dirty gas and product gas vented on change-outs directed to utility boiler.
	38. Spent bed media. Carbons or chars may be combusted in utility boiler. Sulfated metal oxides will require special treatment or burial in sealed pits (life not estimated).
<u>METHANATION</u>	39. Oxygen-free gas circulated in Raney nickel activation.
	40. Vented activation gas. Hydrogen evolved in activation and product gas vented on change-outs directed to utility boiler. Metal dusts generated in catalyst replacement contained in closed filter system.
	41. 130,000 lb/hr condensate from after-cooler directed to waste water treatment. Catalyst replacement and activation will generate metallic solids effluents and caustic liquid effluents which will require special treatment.
<u>COMPRESSION</u>	42. 1000 lb/hr condensate from inter-coolers directed to waste water treatment.
<u>OXYGEN PLANT</u>	43. 425 MM scfd air intake
	44. 330 MM scfd nitrogen and other air constituents. (152 tph oxygen to gasifier).
	45. 85 gpm water condensate from inter-coolers directed to boiler feed-water treatment.
<u>UTILITY BOILER</u>	46. 1060 MM scfd combustion air intake.
	47. 1070 MM scfd flue gas from char combustion, including 10,900 lb/hr SO ₂ . (CO ₂ -18.5%, O ₂ -1.9%, N ₂ -79.4%, S-0.15%). Directed to coal drier, if required for drying coal.
	48. 115-135 tpd limestone to desulfurize flue-gas from char combustion. Scrubber placed on coal dryer exit if flue gas used to dry coal.
	49. 1050 tpd ash and 150-200 tpd sulfated lime from flue-gas treatment. Disposition uncertain, depending on composition, but assume burial in mine or in sealed pits.
<u>COOLING WATER</u>	50. Chemical additives may include chromium or zinc compounds, acids, chlorine, phosphates, phenols, copper complexes.
	51. 2600 gpm water evaporated and 300 gpm drift loss into circulated air if air-fin usage maximized. Early warning system required in return laterals to indicate leakage from process train to control emissions in cooling tower plumes.
	52. Draw-off from cooling towers estimated at 500 gpm. May require special treatment ahead of injection into waste-water treatment. Can be substantially reduced by incorporation of zeolite softening system in cooling water circuit, assuming leakage from process train is very small.
	53. 20,000 MM scfd air circulated against cooling towers.

TABLE 1 (Cont'd)

STREAM IDENTIFICATIONS FOR REVISED SYNTHANE PROCESS

(Stream Numbers Refer to Figure 2. See Text for Details)

SULFUR RECOVERY

- 54. 5 MM scfd regeneration air for Stretford solution.
- 55. Vented regeneration air directed to boiler firebox. 210-220 MM scfd CO₂ containing up to 5 ppm H₂S. may be directed to boiler stack.
- 56. Make-up Stretford solution.
- 57. About 140 tpd elemental sulfur produced for sale. Liquid purge from Stretford will require special treatment.

WATER TREATMENT

- 58. Additives to system may include milk of lime (115 tpd), anti-foam, phosphoric acid (0.5 tpd), sulfuric acid, char (42 tpd), oxygen or ozone, and other agents.
- 59. Up to 230 tpd lime sludge, 76 tpd wet char (recycled to utility boiler), and miscellaneous sludges from aeration, biox and separation facilities. Sludges will require special treatment.
- 60. Aqueous scrubber effluents from dust removal require special treatment, including facilities for separation of ammonia, tars, oils, phenols, and pyridine bases. Up to 160 tpd of ammonia may be separated for sale. Control of noxious evaporative losses in treatment facilities may require special engineering, including floating covers on retention ponds or tanks and/or forced draft.
- 61.

stream would require treatment to remove particulates prior to its discharge. If particulate removal were the only consideration for such a stream, then cyclone separation/filtration or electrostatic precipitation would generally be preferred to scrubbing to conserve water, minimize water treatment loads, and to facilitate recovery of fines. In this case, however, flue gas from the utility boiler will require desulfurization (see Section 3.3.1), so that we have assumed that limestone scrubbing will be used.

On the basis that tar is combusted along with char in the utility boiler, and that flue gas from the boiler would be available at the coal dryer at about 550°F, the utility boiler flue gas stream could dry feed coal containing in excess of 6 weight per cent water. On the basis that limestone scrubbing will be used thereafter to limit SO₂ emission, saturated flue gas leaving the scrubber would carry some 166,000 pounds per hour of water into the atmosphere. To limit SO₂ emission to an acceptable level could require up to 230 tpd of limestone and the net resulting SO₂ emission will be on the order of 5500 pounds per hour.

2.2 Coal Grinding

Approximately 53 MM cfd of atmospheric air is aspirated into the ball-mill grinding operation, which reduces coal size to 70 per cent through 200 mesh. The air stream is heated in a circulation system and passed through the mills, where it serves both to control moisture in the pulverizing process and as transport medium for the pulverized material.

Close control of the milling circuit is required when air is used in this manner to reduce to a minimum operation in the explosive region, such as may obtain at start-up or shut-down of mills. Precautions should also be taken against accidental overheating of coal, as may occur due to mechanical failure of a heated mill. In general, inerting systems are provided for these devices. An alternative might involve use of an inert or low-oxygen gas stream in place of air as, for example, the nitrogen from the oxygen plant or a flue gas.

The coal/air mixture passes through cyclones, where separation occurs, and the air stream is discharged to the atmosphere through bag filters. Such arrangement is commercially proven, with acceptable particulate emission, though load on the filters may amount to some 60 tpd in this case (15). Only trace quantities of hydrocarbons have been detected in such commercial streams, and odor is not considered a problem. Collected fines from the filters are recycled to mill product.

It should be noted that it is possible to effect substantial drying of coal in the milling circuit. Such systems have been designed to accept coals with surface moisture content ranging to 20 weight per cent. But the overall effect is to reduce mill capacity, such that there is normally incentive to predry coal feed to the mills.

Nominal drying capability, amounting to some 2 weight per cent of the gasifier coal feed rate, is estimated for the milling circuit in this design, based on indicated air heater provisions and mechanical energy requirements in the circuit.

2.3 Gasification

2.3.1 Coal Feed System

Coal is charged to the gasifiers in the Bureau of Mines design through pressurized lock hoppers. A number of alternatives regarding the mechanical arrangement, the pressurizing medium, and the consequent net energy requirement and pollution potential of lock hopper operation appear feasible.

In this design, each gasifier is provided with one lock hopper, which discharges alternately into two feed hoppers from which coal is passed to the gasifier using a steam/oxygen mix as transport medium. Oxygen reacts with coal in the transfer line, liberating heat which prevents steam condensation that might otherwise interfere with coal transport. Hence, in this case, some pretreatment of coal occurs in the transfer line.

The gasifier charging sequence involves filling the vented lock hopper from pulverized coal storage bins, pressurizing the filled lock hopper, and discharging its load into a feed hopper. In this configuration, it is presumed that a feed hopper is maintained slightly above gasifier operating pressure while on line to the gasifier, and that pressure is allowed to drop to the gasifier pressure level as the hopper empties. At this point, the feed hopper is ready to accept another charge from the filled, pressurized lock hopper.

The pressurized lock hopper must be vented to essentially atmospheric pressure when empty of coal in order to be refilled. In a multiple gasifier system, operation may be sequenced such that initial venting may be to a lock hopper awaiting pressurization, or to a succession of these, such that some of the energy represented by the compressed gas may be recovered directly, while simultaneously reducing the quantity of residual gas to be vented ultimately. Alternatively, two or more lock hoppers might be provided each gasifier specifically to permit such sequencing, since there may be practical operating limitations to the degree to which gasifier operation may be scheduled.

Another alternative that may be attractive for large systems would involve specific energy recovery in the venting process, as by means of turboexpanders, which may be used to drive compressors or to generate electricity. Obviously, combinations of direct use and specific energy recovery are possible.

The choice of pressurizing medium may directly affect the main gasification processing sequence, as well as the design and operation of the lock hopper system. The use of steam alone as this medium is considered mechanically unacceptable due to interference expected with coal transport from condensation, which may not be controllable.

Since some fraction of the pressurizing medium will travel with the coal into the gasifier, the use of a nitrogen-containing inert gas for such medium is considered unacceptable from a process viewpoint, since it dilutes the product gas, reducing its heating value, and occupies volume in the reaction sequence otherwise.

Direct pressurization from the gasifier, as has been done commercially in the Lurgi system (16), or the use of any combustible gas, as, for example, product gas, is unacceptable, inasmuch as the pretreatment section of the Synthane gasifier must operate in an atmosphere of steam and oxygen. On the other hand, there may be sufficient compression energy credits to warrant consideration of a mechanical arrangement which permits the use of steam only to transport coal from feed hoppers and, additionally, to strip combustible gas from such transferred coal before coal contacts oxygen in the pretreater. And should coal pretreatment not be required in a particular situation, use of raw or product gas for pressurization may be a preferred alternative. It will be necessary then to include means for purging the vented hopper, as by use of steam or nitrogen, before the hopper is opened to be filled.

It is believed that CO_2 , which is separated from the main process gas stream following shift conversion, is the preferred pressurization medium (8,9). Such CO_2 must be superheated to prevent liquifaction at 1000 psia, and the rate of heat loss from the pressurized feed system must be controlled to prevent condensation. Depending on the mode of operation of the feed system, the volume of raw gas issuing from the gasifier may be increased some 3-5 percent as a consequence of admission of pressurization gas with coal. This increased volume must be handled through the acid gas removal step, but it is presumed otherwise not to affect process operation.

The composition of gas vented from the lock hopper can only be surmised at this point, since it will be a function of the method of operation of the coal feed system, including the pressurization medium employed and the properties of the coal in use. It is probable that removal of particulate matter will be required before such gas may be vented to the atmosphere. If combustible gas be employed, it might be recycled to the gasification train via compression, or might be directly combusted in the utility plant.

In the method of operation of the coal feed system described above for this design, there should be no opportunity for gasifier gas to back through the lock hopper. Hence, trace quantities only of coal-originated materials, other than coal dust, should appear in vent gas. However, the use of a heated hopper system, as will be required if CO₂ is the pressurization medium, may subject coal in contact with heated surfaces to sufficiently high temperature to cause stripping of volatiles or of sulfurous gas. Formation of carbon- or carbonyl sulfides is also possible.

It is apparent that CO₂ obtained from the acid gas treatment facility may contain sulfur, as well as small quantities of CO and hydrocarbons. The form and quantity of sulfur in this gas will depend on the sulfur recovery process employed. At Bruceton, from the output of a Stretford sulfur recovery unit, H₂S content of separated CO₂ is indicated to be less than 5 ppm. In the Bureau of Mines prototype pilot plant, this gas, including the lock hopper vent stream, will be incinerated in a thermal oxidizer before being discharged to the atmosphere. This procedure may be directly applicable to the commercial design, i.e., off-gas from the sulfur recovery unit, including lock hopper vent gas, may be sent to the utility boiler where sulfur would be oxidized to SO₂ and the stream would otherwise dilute flue gases from fuel combustion.

We have assumed an alternative to continuous atmospheric venting which involves containment of lock hopper vent gas, as in gas holders from which it could be recompressed, limiting the requirement for fresh make-up gas to the losses (largely back into the system) from the coal feed system. In this arrangement, it will probably be necessary to treat or filter gas entering the holder to remove dust.

It is thus indicated that the only material which may be discharged from the coal feed system will be CO₂, which gas would otherwise have been so discharged from the sulfur recovery unit. The rate at which such CO₂ will be discharged will depend on the degree to which gas is recycled in the feed system, but the system may obviously be arranged such that no gas is discharged to the atmosphere at this point.

2.3.2 Char Letdown

Ash must be removed from the Synthane gasifier, as in most gasification processes, in a more or less continuous fashion, to maintain carbon concentrations in the gasification zone sufficiently high for desired reactions to proceed. Experimental work indicates incentive for limiting the degree of carbon gasification, and a proposed feature of the Synthane process involves setting the carbon content of the ash (char) removed from the gasifier such that combustion of the char will balance the total steam and energy requirements for the process.

The high operating pressure of the Synthane gasifier imposes special problems on the system used to extract char. At the point of

discharge from the gasifier bed, char is indicated to be at temperatures in excess of 1700°F.

The char in this design represents a significant sensible heat discharge from the gasifier. From thermal and process points of view, perhaps the ideal system would transfer hot char directly to the boiler in which it is to be combusted along with any associated gas, preserving most of this heat and avoiding use of cooling media, water or steam, that would require additional energy to subsequently separate or treat. The mechanical design of a throttling arrangement that would permit such operation, however, will require substantial development.

Consideration of a variety of alternatives led the designers of the large pilot plant (9) to a system wherein char is cooled in situ prior to the point at which it must be passed through valves. Hot char is caused to flow into a separate fluidized bed cooler by regulating the pressure differential between the gasifier bed and the cooler. Steam is used to fluidize the bed, and water is injected into the system for cooling. High-pressure steam is generated in the cooler, and this steam may be used in the process (specifically in the carbon monoxide shift converter) after it has been filtered to remove char fines. The designers point out that this steam might be directed to the gasifier in its contaminated state if the gasifier distributor were designed to introduce contaminated steam and oxygen separately.

Cooled char may be fluidized out of the cooler bed into lock hoppers, avoiding throttling valves, or may be passed from the bottom of the cooler bed through valves into lock hoppers. Agglomerates which may come from the gasifier could present problems with either method of cooler operation.

The preferred alternative is a "dry" system, in which a filled char lock hopper is isolated with valves which are arranged to be blown clean before closing. Steam is vented to atmosphere via filters arranged within the lock hopper, ahead of the pressure-reducing valves. Char flows out of the bottom of the lock hopper into a conveying line in which steam is used as transport medium. The empty lock hopper is repressurized with steam before being put on line to again receive char.

A second alternative directs a char/steam mix from the cooler through a slide valve into a char slurry quench tank, where water sprays cool the char and a slurry is formed. The quench tank is vented to the char cooler. Char slurry is depressured through orifice/valve arrangements, the char slurry is filtered to recover water, and water is recycled to the slurry quench tank through coolers. The char filter cake is estimated to contain 40-50 per cent water in this case.

Gas from the gasifier will be carried into the char cooler along with char. It is presumed that most of this gas will issue from the char cooler along with the generated steam and be directed back into the main gasification stream, either directly into the gasifiers or at

the shift converters. It is not possible to estimate the degree of gas contamination that may persist through the char depressurizing system into the steam which is indicated to be vented ultimately from a "dry char" process. Some 3000 pounds per hour of steam is estimated to be so vented if this scheme be applied to the Bureau of Mines design. Depending on its composition, some of this vent steam may be employed in the scrubber water treating system, or may serve to transport char to the utility boiler, in an integrated commercial plant. Although there would probably be least atmospheric pollution associated with a "wet char" or slurry letdown system, the water pollution generated and the energy associated with water treatment and wet char combustion would indicate that the slurry technique would be used only if an operable dry char arrangement cannot be developed.

To summarize, the design basis (10) does not specify the method by which char will be removed from the gasifiers, except to provide lock hoppers to receive char. The lock hopper volume provided is not consistent with estimates of char density, so that lock hopper cycle rate may be higher than indicated.

With the preferred dry char process, we have assumed that about 100,000 pounds per hour of high pressure steam will be generated by direct water injection in the char cooler, and that this steam, along with associated gasifier gas, will be reintroduced into the process at the shift converters. Some 3000 to 6000 pounds per hour of steam is estimated to be vented from the lock hoppers, depending on cycle rate. "Dry" char is assumed to be conveyed to the utility boiler using a steam transport system. Net atmospheric pollution associated with char let-down is therefore assumed minor.

2.4 Dust Removal

Raw gas issuing from the gasifiers must be treated to remove particulates and condensable matter that may interfere with subsequent gas processing. The precise nature of materials which must be separated from raw gas at this point is not known, except that coal or char fines and coal-tars or oils are assumed to be present.

In the design basis, gas from the gasifiers passes firstly through cyclones, where heavier particles (char) are removed, and then the gas is subjected to cold-water scrubbing (see Figure 3). Scrubber liquor effluent is depressured into decanters, where tar separation occurs, and water is recirculated to the scrubbers through water-cooled heat exchangers by high-pressure pumps. This design does not further detail the operation, or provide for further handling of separated products or of scrubber liquid.

This gas clean-up process has not been experimentally demonstrated. Laboratory procedure (17) at the Bruceton laboratories of the Pittsburgh Energy Research Center (PERC) has generally involved passage of gasifier effluent through dust filters and a series of water-cooled condensers, wherein dusts, tars, and water are condensed from gas prior to pressure reduction.

FIGURE 3
DESIGN BASIS DUST REMOVAL (10)

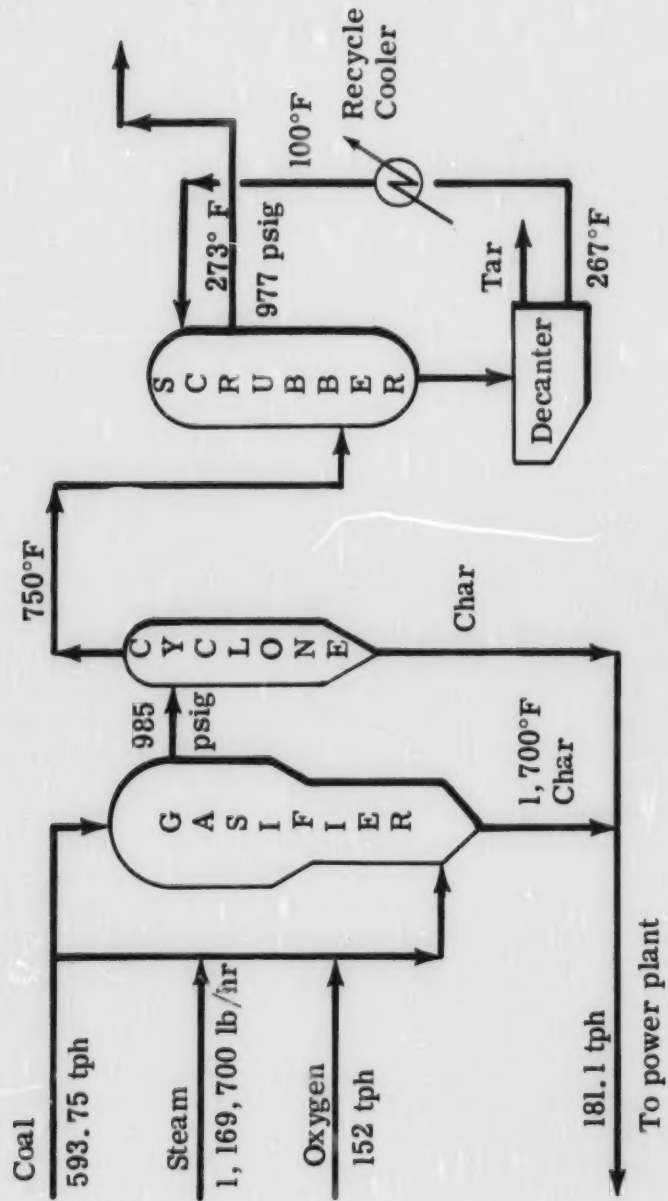
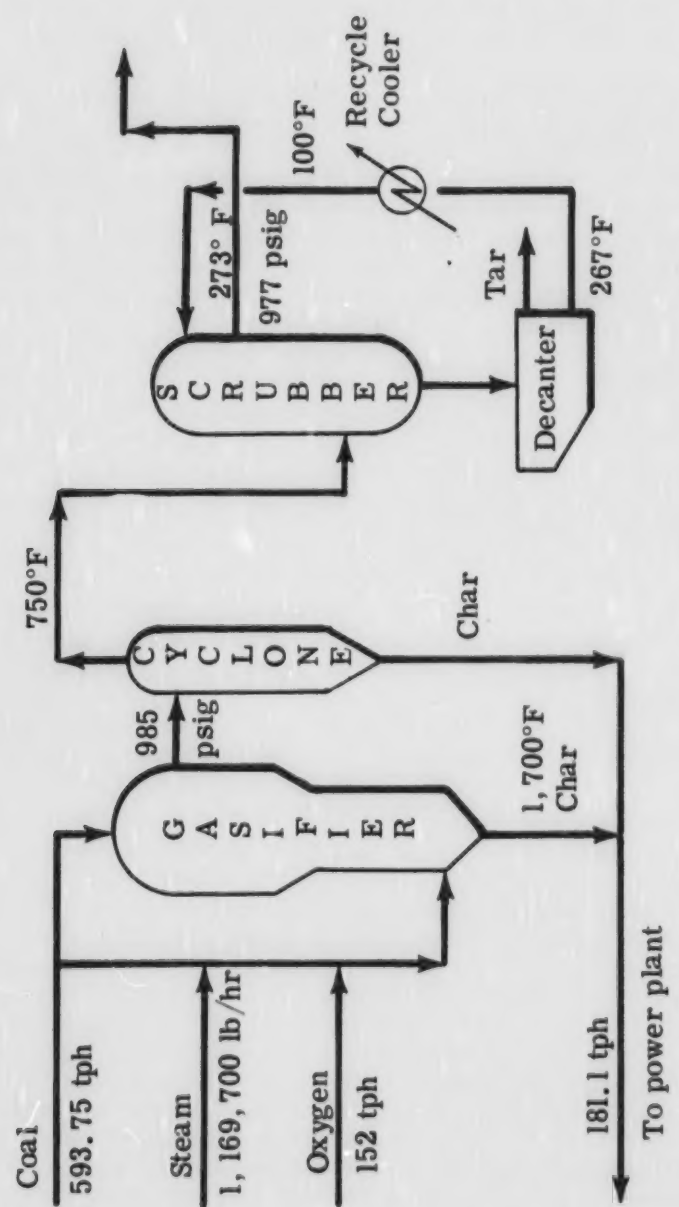


FIGURE 3
DESIGN BASIS DUST REMOVAL (10)



Prior art would indicate that the gas clean-up procedure outlined in the Synthane design will require substantial development from both process and pollution view-points. As proposed, the operation is a significant energy and cooling water consumer. The physical operation of "dry" cyclones is by no means assured in this system.

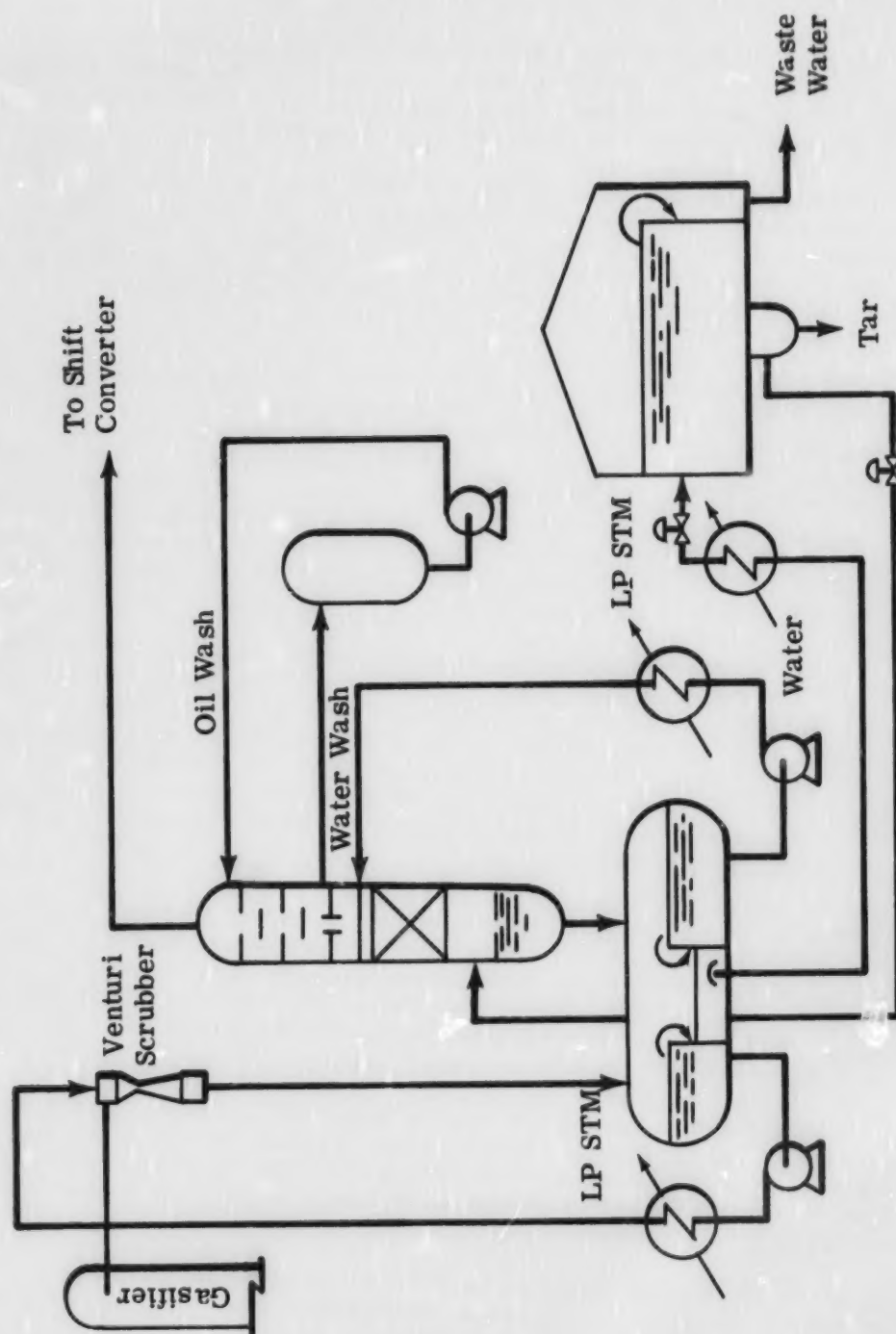
Provision has not been made to contain and recover gas which will be carried out of the scrubbers by the scrub liquor, and which will separate from the liquor as this stream is depressured in the decanters. The implied method of operation of the decanters would almost certainly lead to emulsion formation in these vessels. And the distribution of solid and liquid phases in these vessels otherwise is impossible to assess. It is further not clear whether water scrubbing alone will suffice to clean gas of all material which may affect downstream processing.

The designers of the prototype pilot plant have accordingly provided a flexible system (18) which addresses many of these questions in a manner by which it is hoped to obtain the experimental data required to design a commercial plant (see Figure 4). In the pilot plant, gas from the gasifier passes firstly through a venturi water scrubber where bulk cooling occurs. Venturi scrubber effluent is directed into a baffled high-pressure surge tank where gross separation of particulates takes place. The same surge tank is arranged to serve as reservoir for a separate high-pressure scrubber tower. Low-pressure steam may be generated in the process of cooling recycled effluents to the venturi scrubber and to the scrubber tower from the surge tank. The scrubber tower is arranged so that water and/or oil may be used as scrubbing media. Effluent from the high-pressure surge tank is depressured into a low-pressure decanter, where final phase separation occurs.

This system resembles the processing sequence employed by Lurgi and others in low-temperature coal carbonization plants constructed in Germany prior to and during World War II. The Lurgi-Spülgas installation at Offleben (49) utilized a waterspray and rotating screen to first remove dust and heavy tar from gases leaving the carbonizing ovens. Light tars and "middle oil" were condensed in sequence, and the removal of condensable material was completed in mechanised wash-oil scrubbers which recovered "benzine".

This same gas-treating sequence was adapted to the Lurgi-pressure coal gasification process (24). Both hand-operated scrapers and water sprays were required to maintain offtake passages through which gasifier gas issued (at 575°F and 20 atm.) into a water spray cooler. Heavy tar which condensed was discharged through a trap, and water was recirculated to the sprays through external coolers. The gas stream exited the cooler at about 300°F. Operation of the spray cooler is however indicated to have been troublesome due to tar-water emulsification, and the spray coolers at Bohlen, for example, had undergone four or five design revisions (24).

FIGURE 4
RAW PRODUCT GAS SCRUBBING (9)



Lurgi designs (23,24,50,61) place the direct-contact water quench cooler immediately on the gasifier vessel, minimizing the potential for deposition in the gas off-takes. It is apparently not practicable to extract high-level energy from this gas quenching process.

We believe it may be possible to adapt a "tar-scrubber" of the type developed for petroleum fluid coking reactors (46,62) to the Synthane coal gasifier to avoid the mechanical problems associated with tar and solids deposition in the gas outlets. Moreover, it should be possible to extract high-level energy from the process. The configuration for this arrangement is shown in Figure 5.

In the fluid coker, the scrubber vessel is integral with the coker reactor. The cyclone is internal to the reactor, with its outlet gas discharge into the scrubber. Heavy tar condensed from the gas stream in the scrubber is pumped through external exchangers, where high-pressure steam is generated. The cooled tar stream separates, with the portion not used for scrubbing being returned to the coker feed line. It is of course necessary to control temperature of the tar pool in the bottom of the scrubber vessel and tar velocities in the external circuit to prevent coking and solids deposition.

In the Synthane design, gasifier outlet temperature is estimated to be 800-1400°F. A steam dew-point of about 440°F is estimated for the raw gas conditions. It is further estimated that up to 70 percent of the heavy tar in the gas stream may be condensed by operation of the tar scrubber at about 560°F (63), or sufficiently high in temperature to permit generation of 1000 psia steam in the external circuit. It is estimated that about 365,000 pounds per hour of 1000 psia steam could be generated in this manner, assuming gasifier output to be at 1000°F.

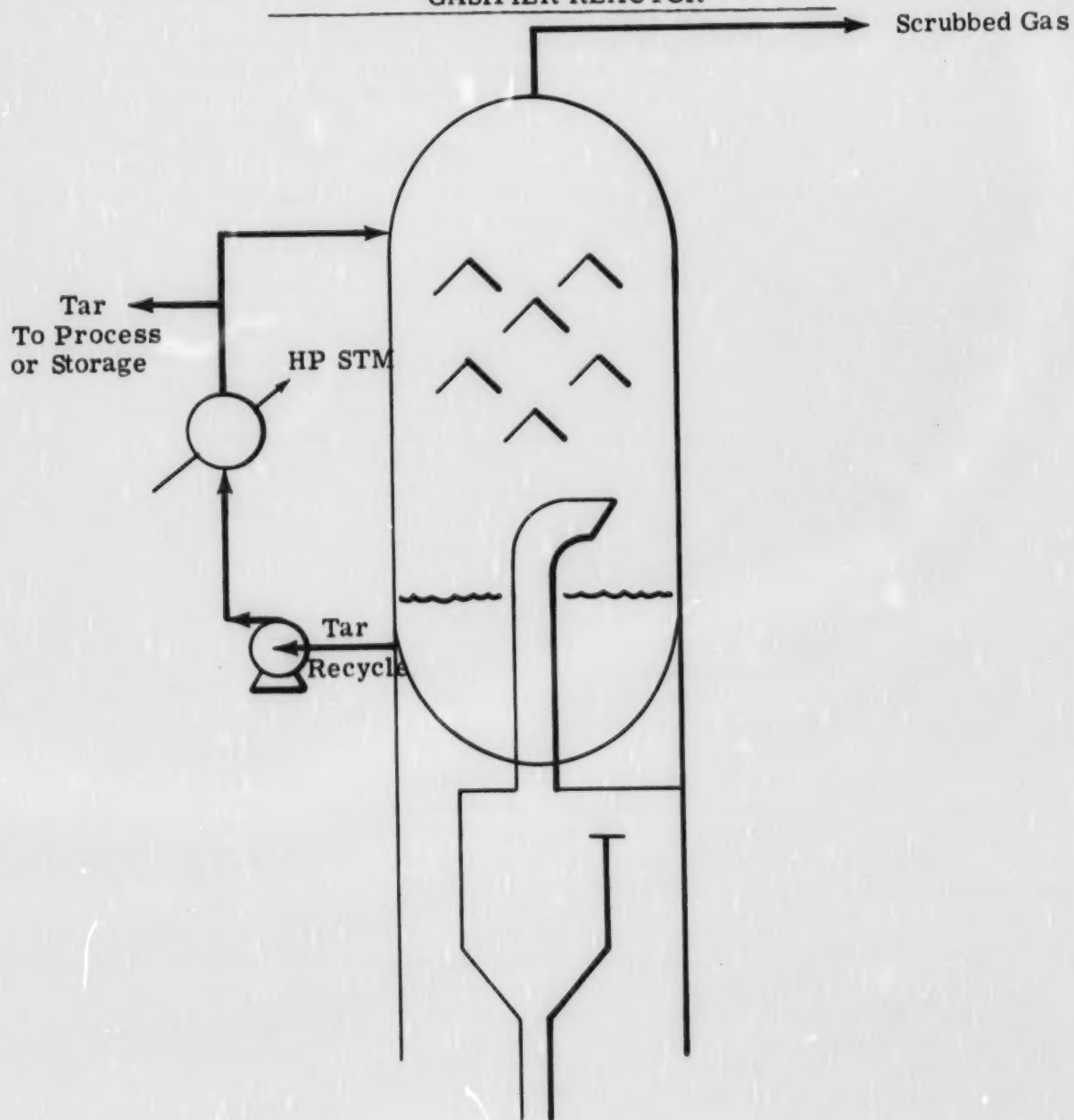
Removal of the bulk of the heavy tar in the gas stream at this point should greatly reduce the emulsification problem as water is condensed from the gas downstream. Similarly, the tar scrubber would serve to remove a major fraction of the char, ash, and coal fines contained in this gas, so that loads on the downstream tar-oil separation and water treatment systems should be reduced significantly.

From a thermal point of view, it would be desirable to return the separated tar stream to the gasifier, as is done in the petroleum coker. But if this is found to adversely affect gasification, such separated tar could instead be directed to the char utility boiler (see Section 3.3.1) or may be further processed for sale.

It is recognized that the mechanical arrangement at the coal gasifier reactor head is more complex than is the case for a petroleum coker, in that the coal feeding arrangement must be accommodated. It should be possible, however, to offset the coal feed system.

FIGURE 5

**TAR SCRUBBER SHOWN INTEGRAL WITH
GASIFIER REACTOR**



It would also be possible to design a single combined scrubber-fractionator tower which would separate tar, oil, and naphtha in sequence up the column. Economies effected in scrubber-fractionator vessel costs must, however, be balanced against the added structural costs associated with the placement of a tall structure on top of the gasifier. Hence a succession of scrubbers, similar to the tar scrubber, but operating at successively lower temperatures, and generating steam at successively lower pressures, might be used to clean gas ahead of the shift converters. What must yet be defined, however, is the limiting temperature of gas at the outlet of such a scrubber train, or the limiting contaminant levels in gas that will not interfere with the shift conversion. The Westfield Lurgi plant (23) was able to operate its shift reactors satisfactorily (at 350 psig) on gas which had been cooled to 310°F.

To the extent that water vapor need not be condensed from gasifier effluent or that gas be cooled below about 800°F in the process of cleaning gas, there is net thermodynamic advantage to the process, since both additional heat and water (supplied as high-pressure steam) are otherwise required in the succeeding shift conversion reactors. Hence an ideal system would remove contaminants in gas only by cooling to about 800°F, generating steam in the process. Alternatively, shift conversion catalysts and procedures might be developed to tolerate carbon-containing contaminants still present in gas from such "dry" cleaning process. Gross contaminant removal would then follow shift conversion, at which point the total product gas stream must be cooled to effect acid gas removal in any case.

Even if a more nearly ideal system is not developed, the commercial design will almost certainly include heat recovery facilities at this point. Energy recovery in the depressurizing step may also be practical, as by use of turboexpanders on gas, or hydraulic turbines or flow-work exchangers (19) on liquids.

In this design, we have assumed that scrubbing will be used following the tar scrubber, but that gas which separates from the scrubber effluents on depressuring will be recompressed back into the main gas stream at a point following shift conversion. Additional tar and hydrocarbons which condense along with water from the gas stream as the stream temperature is lowered may be directed to finishing facilities to be processed for sale, or could be burned in the utility boiler. Either or both water and light hydrocarbon might be recirculated to scrub the gas stream, and steam could be generated in the process of cooling the circulated fluids. Alternatively at some point, gas would be sufficiently clean to permit direct operation in a conventional waste heat boiler. On the assumption that gas temperature is reduced to about 300°F to effect clean-up, some 300,000 to 400,000 pounds per hour of low-pressure steam may be generated in the scrubbers.

The degree of saturation of scrubber effluent with respect to any given gas component will depend on operating parameters that have yet to be defined. Methane, hydrogen, H_2S , and carbon monoxide evolutions from water at indicated conditions and rates could each amount to 400-1000 scfm, for example. CO_2 evolution might be twenty times as much, so that the total gas stream could amount to 20-30,000 scfm, or to 30-40 MM scfd. Gas may also be physically entrained out of the scrubbers in the liquid effluent streams.

Hence, although there may be mechanical and corrosion problems associated with design of a suitable gas/liquor separator and with compression of separated gas, the net effect should be that no gas issues to atmosphere in the dust removal process.

2.5 Shift Conversion

Scrubbed raw gas from the dust removal process is separated into two equal streams, one of which by-passes the shift converters, since only half of the total stream must be shifted to adjust the total $H_2:CO$ ratio to 3:1 for purposes of methanation. In this design, a significant quantity of high-pressure steam must be introduced to the catalytic shift converters to achieve desired equilibrium, however.

The shift conversion is a totally-contained procedure, so that no effluents issue to atmosphere.

2.6 Waste Heat Recovery

The raw gas streams which are split ahead of shift conversion are recombined following the converters, and are cooled from an average temperature of about $500^\circ F$ to $300^\circ F$ ahead of the gas purification system. Low-pressure steam is generated, and there are no effluents to atmosphere.

2.7 Light Hydrocarbon Removal

We have considered that it may be desirable to treat the combined gas stream at this point to remove condensable hydrocarbons to minimize contamination of the Benfield system. It may however prove practicable to defer such treatment until acid gas has been removed, an alternative which may be thermally preferable if the main gas stream is to be cooled to a low temperature after acid gas removal. A number of considerations are involved, including the ultimate disposition for hydrocarbons which are separated (whether processed for sale or consumed as fuel), the effect of hydrocarbon contamination on the method by which the acid gas stream is treated, including the desulfurized residual, as well as the direct effect on the Benfield system. There will be considerable relevant commercial experience with the Benfield acid gas removal system to enable a designer to assess the direct effect by the time more precise values for the gas composition become available.

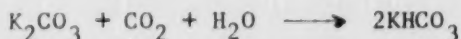
For our design, we have assumed that the gas stream may be cooled in water exchangers to about 90°F after it has been used to reboil the Benfield regenerator and passed through light oil scrubbers to remove B-T-X components. The scrubbing fluid would be available from the upstream hydrocarbon separators. Gas which separates on depressurizing this scrubber effluent could be recycled to the vapor space of the upstream separators for recompression into the main gas stream. Downstream distillation facilities would be required to separate naphtha if it were to be sold. It is estimated that 20,000-25,000 GPD of B-T-X could be so separated, requiring an estimated equivalent of 25,000 pounds per hour of low-pressure steam.

Part of the heat removed in the cooling process could be returned to the gas stream after scrubbing by exchange with the heated water leaving the coolers, so that the net thermal loss might be held to the equivalent of about 60,000 pounds per hour of low-pressure steam. About 18,000 pounds per hour of water would be condensed from the gas stream on cooling, and this (equivalent) water would have to be reintroduced on reheating the gas to avoid depletion of the Benfield solution. This might best be accomplished by direct introduction of high-pressure steam, rather than by reintroduction of the contaminated separated water, which would be directed to the waste water treatment facility.

2.8 Gas Purification

The gas purification or acid gas removal process which is used is the "Benfield" hot potassium carbonate system developed by the Bureau of Mines (20,21,22). This method of removing CO₂ and H₂S from the produced gas is indicated to have substantial thermal advantage over amine systems at the high process pressure employed.

In the Benfield system, gas absorption takes place in a concentrated aqueous solution of potassium carbonate which is maintained at above the atmospheric boiling point of the solution (225°-240°F) in the high-pressure absorber. The high solution temperature permits high concentrations of carbonate (alkalinity) to exist without incurring precipitation of bicarbonate according to:



Partial regeneration of the rich carbonate solution is effected by flashing as the solution is depressured into the regenerators. In this design, sensible heat of the main gas stream is used to reboil the regenerators, so that the gas is cooled to about 260°F in the process. The gas is further cooled in cold-water exchangers to about 225°F before entering the absorbers (but see Section 2.7 above).

It is necessary in this design to admit additional low-pressure steam into the regenerators to complete the regeneration process and to balance heat and water requirements. Regenerated solution is pumped back through the absorbers. The main process gas stream exits the absorbers at 230°F, and is cooled by cold-water exchange to about 100°F before undergoing residual sulfur cleanup. Stripped acid-gas flows to the sulfur recovery plant.

Most of the reported experimental work related to this process was performed at a total absorber pressure of 300 psig (22) on clean gas mixtures. There is therefore some degree of speculation regarding extrapolation to the gas mix and high operating pressure of the Synthane process. At least one successful commercial application of this process in a Lurgi gasification plant has been reported (23). In this case, absorption takes place at about 284 psig. Feed gas contains about 36 volume per cent CO₂ and about 300 grains H₂S/100 ft³. CO₂ concentrations in outlet gas is two percent and H₂S concentration is about five grains/100 ft³. Corrosion problems have been encountered with the liquor circulating pumps in this system, but inhibiting additives have apparently been partially successful in this regard.

The Bureau's own work indicates that methane and CO are about one-fifth as soluble in concentrated K₂CO₃ solution as they are in water at comparable partial pressures and temperatures, and that hydrogen is about one-third as soluble in carbonate (22). The loss of product gas into the acid gas stream is a consideration in any acid gas removal process. For this design it is estimated at about 0.5 per cent of the plant output, assuming saturation of the absorber liquor.

The combination of high-pressure absorption and low-pressure regeneration is a suitable case for consideration of mechanical energy recovery. Comments relative to energy recovery at the dust removal step (see above) are also pertinent here. Incentives for development of such systems escalate with plant size. The economic balance in any such attempted improvement must include factors related to development costs and added process complexity and operating hazards, as well as the first cost of required hardware.

There should be no discharge to the atmosphere from the gas purification plant.

2.9 Residual Sulfur Cleanup

Methanation catalysts are adversely sensitive to very small quantities of sulfur in feed gas. The Benfield system is reported to be capable of operation such that sulfur present in process gas as hydrogen sulfide and carbonyl sulfide may be virtually completely removed. Less is known about the other forms of organic sulfur which may be present in process gas, especially thiophenes.

This design incorporates a sequence of iron oxide and char towers for residual sulfur cleanup ahead of the methanation reactors. There is a long history of the use of such materials to clean synthesis gas (24,25,26). It is estimated that total sulfur in gas may be reduced to less than 0.1 grain/100 ft³ in this arrangement.

There is, however, no clear basis for estimating the life of these beds, and hence no indication of whether the intent is to dispose of spent material or attempt regeneration. The designers of the prototype plant have elected to reverse the order of treatment, placing the activated carbon bed ahead of the sponge iron tower. In this case, activated carbon is meant to be regenerated regularly with steam, and sponge iron discarded when spent. Reported experience (24) indicates that temperature rise may be excessive in an activated carbon bed if H₂S content of feed gas exceeds about 650 ppm, as may occur in this case with an upset in the Benfield system. It is also reported that gum formers, dienes, indene, and styrene, if present, may interfere with recovery of H₂S on carbon. The steam stream used to regenerate the carbon bed may be directed back to the Benfield regenerator, or, if contaminants are troublesome, could be directed to the utility boiler for disposal. Some provision will have to be made to permit change-out of the beds in this section. Hence, the high-pressure gas in the beds will have to be vented, and the beds will have to be inerted before being opened. It is assumed that the vented high-pressure gas will be directed to the utility boiler. Steam, which may be used for inerting, may be directed back to the Benfield regenerator.

Steaming, or other inerting, will also be required to purge the bed of oxygen when a new bed is to be put on line. It is assumed then that the only discharge to atmosphere from this section will be such inerting medium, and, further, that the quantity of this gas will be very small.

2.10 Methanation

The Bureau of Mines has developed two methanation processes for application in the Synthane system, (6, 7, 27) and both will be tested in the prototype pilot plant being constructed at Bruceton.

This design incorporates the Tube Wall Reactor or TWR process, in which the methanation reactor is constructed in the form of a heat exchanger. Reaction occurs on a Raney nickel catalyst coating applied to the exterior of the exchanger tubes, and Dowtherm is vaporized through the tubes to remove reaction heat. High-pressure steam is generated in a separate boiler in the process of condensing and cooling the Dowtherm heat exchange fluid, which is then recycled to the methanator.

The Bureau has developed techniques for coating the inside of tubes with catalyst, an arrangement which may be more amenable to scale-up, simplifying catalyst replacement. At this point, the expected life of catalyst in this system is not known. Most of the experimental data reported (8) was obtained at 300 psig, so that additional development is required to redefine the process at Synthane process pressure ($\sim$ 930 psig). Catalyst life targets early on in the development were set at 2000 hours.

The Hot Gas Recycle or HGR methanation process also uses Raney nickel as a catalyst, but the catalyst in this case is deposited on an element consisting of closely-spaced parallel plates installed in a high-pressure shell. The Dowtherm, or separate heat-exchange fluid, is avoided in this system by employing the process gas at very high recycle rates through the methanator to limit temperature rise. The physical configuration of the methanation reactors is considered more suitable for commercial scale-up in this arrangement, but the process carries energy debits relative to TWR methanation, and the design of compressors for gas in this pressure-temperature regime will require development.

When on-line, there should normally be no atmospheric discharge from the methanation section. As in the case of the fixed-bed sulfur clean-up facilities discussed above, however, provision must be made for taking methanation reactors out of service for catalyst replacement. Hence, the reactor must first be vented of high-pressure gas. Depending on the size of plant and the frequency of change-outs, it may prove desirable to provide facilities for recompression of this gas back into the product gas stream. Alternatively, the vented gas could be directed to the utility boiler. Inerting of these vessels prior to opening them might best be performed with nitrogen (supplied from the oxygen plant), and, in this case, the inerting effluent stream would be directed to the boiler.

If Raney nickel is employed as catalyst, it is presumed that facilities for activating the catalyst, if not, in fact, for complete removal and replacement of catalyst on supporting surfaces, will be provided on-site. Hence, when a tube bundle of the TWR process, or a catalyst element in the HGR system, has been readied for reactivation, a dilute sodium hydroxide ($\sim$ 2 per cent by weight) solution is passed over the element, and the temperature is raised to about 95°C. Hydrogen is evolved in this process, and this stream might be handled in the same way as high-pressure vent gas. The catalyst element must then be washed free of caustic, using quite pure (distilled) water. Finally, the catalyst system is dried and its temperature raised by circulating hot, oxygen-free gas, such as nitrogen. It is assumed, then, that only this last (wet) nitrogen stream may be discharged to the atmosphere from the methanation section.

Of course, if on-site facilities are additionally provided to remove spent catalyst from supporting surfaces and to re-apply new

catalyst, then suitable arrangements must be provided to contain metal dusts that may be generated in preparing the surfaces for recoating, applying bonding agents (nickel aluminide), and flame spraying of new catalyst.

2.11 Final Methanation

The design basis does not include specific equipment for limiting CO content of product gas issuing from methanation. Depending on the ultimate use of product, CO content may be required to be held to less than 0.1 volume per cent.

As indicated above, the methanation process which will be ultimately commercialized has not yet been defined. However, the experimental data reported to date would indicate that a final treat will be required to limit CO content in methanator effluent to specification. In a commercial plant, some arrangement, possibly involving standby methanators, would probably be required in any event to handle sudden loss of activity or other malfunction in the process train at this point.

In the prototype pilot plant, based on Bureau of Mines experiments, the designers have included fixed bed reactors containing pelletized methanation catalysts (nickel oxides on aluminates) to reduce CO content to specification. Although this procedure may be amenable to scaleup, an integrated method for adjusting temperature of feed gas, and controlling temperature within the beds, must be developed. Procedures for changing out such beds, following along lines discussed above, should result in only small discharges of inerting gas to atmosphere.

In our design, we have assumed that specification CO levels will be achieved in the methanation plant proper.

2.12 Final Compression

Pressure drop through the Synthane train is indicated to amount to about 65 psi. Gas leaving the methanation plant is cooled to 100°F to remove water, and is then compressed to 1000 psig, the design product delivery pressure.

3. EFFLUENTS TO AIR - AUXILIARY FACILITIES

We have elected in this study to treat the main gasification stream separately from all other facilities, which are thereby defined as auxiliary facilities. The functions of these auxiliary facilities are nonetheless required by the process, and, for economic and/or ecologic reasons, would be constructed along with the gasification system in an integrated plant. These effluent streams are also shown in Figure 2, and streams are identified in Table 1.

3.1 Oxygen Plant

The oxygen plant provides a total of 3650 tons per day of oxygen. The only effluents to the air from this facility should be the components of air, principally nitrogen. About 330 MM scfd of nitrogen will be separated. Some of this nitrogen may be used to advantage in the plant to inert vessels or conveyances, to serve as transport medium for combustible powders or dusts, as an inert stripping agent in regeneration or distillation, or to dilute other effluent gas streams. It will be possible to generate about 900 KW of electricity by recovering the compression energy of the nitrogen through turbo-expanders.

About 425 MM scfd of air is taken into the oxygen facility. Placement of the oxygen facility will depend in part on the desire to maintain the quality of the air drawn into the system and, especially, to minimize interference from plant effluents.

3.2 Sulfur Plant

The type of plant used for removal of H_2S from the acid gas overhead from the Benfield regenerators has not been specified in this design. Originally, sulfur removal was to have been accomplished by means of a direct oxidation Claus unit incorporating a tail-gas scrubber using lime or soda ash (18). However, the performance of the Claus system with the relatively low H_2S concentration in the feed gas (about 2-3 weight per cent) could not be guaranteed. Moreover, the desire to use sulfur-free CO_2 from the sulfur plant to pressurize the coal feed lock hoppers (see Section 2.3.1) required that residual H_2S in such gas be considerably below the level that might be achieved by the Claus system. Hence, use of the Stretford process has been assumed for sulfur removal (28).

In the Stretford process, sour gas is washed with an aqueous solution containing sodium carbonate, sodium vanadate, anthraquinone disulfonic acid, and a trace of chelated iron. The solution reaches an equilibrium with respect to CO_2 , such that only small amounts of CO_2 are removed from the gas undergoing treatment.

In this system, H_2S dissolves in the alkaline solution, and may be removed to any desired level. The hydrosulfide formed reacts with the 5-valent state vanadium, and is oxidized to elemental sulfur. The wash liquor is regenerated by air blowing, wherein reduced vanadium is restored to the 5-valent state via an oxygen transfer involving the ADA. The sulfur is removed by froth flotation and filtration or centrifugation. The process may be effectively operated at any pressure up to 1000 psig (29, 30).

The fate of carbonyl sulfide and other organic sulfur compounds which may be contained in the main product gas stream is not now clearly understood. Hence, although it has been indicated that COS is removed from gas by the Benfield system, it is not certain whether and to what degree COS and other sulfur compounds may appear in the acid gas overhead from the regenerators. The Stretford system is indicated to be only partially useful for the removal of organic sulfur compounds. Hence the preferred treatment route for acid gas must await more definitive information related to operation of the Benfield system at high pressure, and especially to Synthane gasification of high sulfur coals.

It should also be noted that the developers of the Stretford system have disclosed (31, 32) processes which convert organic sulfur compounds in hydrocarbon streams to H_2S , as by treatment with steam over U_3O_8 - containing catalyst, which H_2S may then be removed in a Stretford system. As has been indicated elsewhere, the technology of sulfur removal is advancing rapidly, so that it may be expected that improved procedures will have been demonstrated by the time coal gasification finds much commercial application.

About 210-220 MM scfd of CO_2 containing less than 5 ppm H_2S will be separated at the sulfur plant. Depending on the relative economics, the H_2S content of this stream may be reduced to less than 1 ppm in the Stretford system prior to discharge to the atmosphere. We have assumed that the stream will instead be directed to the utility boiler to undergo incineration and treatment along with flue gas.

The air stream used for regenerating Stretford solution is another effluent to the atmosphere from the sulfur plant. This stream is estimated to amount to some 5 MM scfd. This stream is also directed to a boiler firebox.

3.3 Utilities

3.3.1 Power and Steam Generation

The choice of fuel for the generation of the auxiliary electric power and steam required by coal gasification plants markedly affects the overall process thermal efficiency. It is generally least efficient to burn the clean product gas for this purpose. On the other hand, investment in power-plant facilities, including those required to handle the fuel and to treat the flue gas, is generally least when product gas is so used.

Synthane gasification is one of the class of coal gasification processes which generate a carbon-containing char. Research to date would indicate that it is not desirable to gasify more than about 90% of the carbon in feed coal, and that it may be preferable to limit gasification to about 60-70 per cent of carbon for most feeds. A particular feature of the Synthane process design, therefore, is that the carbon content of char leaving the gasifier may be adjusted such that the subsequent combustion of the char will balance the power and steam requirements for the system.

Char generated by the Synthane process is a much more refractory material than feed coal, and generally contains a significant fraction of the sulfur in the original feed(11). Composition of the char produced by the present design is not specified. Several analyses for char generated from the pilot gasification of a Pittsburgh seam coal have been reported:

Table 2

CHARS FROM SYNTHANE GASIFICATION
OF PITTSBURGH SEAM COALS (WT. PERCENT)

	<u>No. 1 (33)</u>		<u>No. 2 (47)</u>	
	<u>Feed Coal</u>	<u>Char</u>	<u>Feed Coal</u>	<u>Char</u>
Carbon	75.7	71.4	68.4	68.9
Hydrogen	5.3	0.9	4.7	1.0
Oxygen	8.3	1.8	9.3	1.7
Sulfur	1.6	1.5	1.3	0.2
Nitrogen	1.5	0.5	1.2	0.5
Ash	7.6	23.9	15.1	27.7
Volatile Matter	-	-	30.9	1.6

It is otherwise indicated, however, that the composition of the char generated may be quite variable, depending on the feed coal and on the operation of the gasifiers (11), so that the combustion properties of char may likewise vary.

Experience with the large-scale combustion of char is so far limited. The Bureau of Mines has reported on one investigation (34) utilizing a specially-constructed dry bottom unit designed to simulate the performance of an industrial steam-generating furnace. In general, it was found that volatile matter content in excess of 20 per cent was necessary for combustion of chars in this apparatus in the absence of a more volatile supplemental fuel (natural gas was used as supplemental fuel). Carbon combustion efficiency was likewise found to be a function of the volatile matter content of char, ranging from 94 to 99 per cent for volatile contents from 5 to 15 per cent. More supplemental fuel was required for the least volatile chars to maintain flame stability.

Hence, it may be assumed that combustion of Synthane chars will be possible in conventional fireboxes if product gas is used as supplemental fuel. This alternative might be preferred then on the basis of carrying the least developmental debits, and because it should be possible to adjust SO_2 concentration in flue gas from most chars such that subsequent flue gas treatment may be avoided. It has the disadvantage of adversely affecting overall thermal efficiency.

A large number of power plant fuel alternatives involving combinations or separate use of feed coal, char, tar, raw gas, or product gas are open to the Synthane plant designer. It would appear that conservation would dictate that carbon contained in generated char should be recovered, as by use of char as fuel. But an alternative that may be available would be to gasify Synthane char in a Koppers-Totzek gasifier (14) or its equivalent, producing a low-Btu clean gas, which may then be consumed separately or in combination with one or more of the other available fuels to produce power. Since all auxiliary facilities will have been otherwise provided for the Synthane plant, the addition of gasifier(s) for char may be a preferred alternative should char combustion boiler development show particular problems, as with fouling, corrosion, stability, or sulfur removal.

For this design, we have assumed that equipment will be developed to combust char alone with essentially complete carbon utilization. This may be possible, for example, in a fluidized bed boiler and, especially, in a fluidized bed system which incorporates combustion in the presence of limestone to remove sulfur (35). Otherwise, such char combustion will in general require that flue gases be treated to remove sulfur. And, as indicated above, the development of a large-scale char burning system, as with the development of any new commercial boiler concept, may involve appreciable effort, a long lead time, and considerable investment.

At least one other power plant fuel combination deserves mention. Tar removed from the gasifier output might be combusted along with char, providing the supplemental volatile matter that may be required to achieve stable combustion. This alternative suffers mainly from the sulfur removal problem presented by such combustion. Moreover, tar should be valued higher than feed coal as fuel, so that feed coal might more properly be used as supplemental fuel if required for char combustion. The present design assumes that produced tar will be sold, and credits the thermal balance with the fuel equivalent. In the light of current petroleum availability and pricing, it may well develop that tar may be marketable. Again, it may be possible to gasify tar along with char in a suitable gasification unit to produce clean gas, avoiding stack gas treatment entirely and greatly reducing boiler investment.

In the present design, 4350 tpd of char is combusted in the utility boiler. If char of the composition (1) above is assumed, and if combustion be effected using 10 per cent excess air, 1060 MM scfd of combustion air will be required. The volume of flue gas from the combustion will amount to some 1070 MM scfd, assuming feed char to be dry, that carbon combustion efficiency is 100 per cent, and that all of the sulfur is converted to SO_2 , i.e., no sulfur remains in ash.

A higher heating value of 11,000 Btu per pound is estimated for char of this composition, so that the hourly firing rate amounts to some 3980 MM Btu. Unfortunately, there will also be emitted some 10,900 pounds per hour of SO_2 or about 2.7 pounds SO_2 per MM Btu. Hence flue gases must be treated on the basis of current standards to reduce emitted SO_2 to less than 1.2 pounds per MM Btu (36). The theoretical limestone requirement for this purpose amounts to some 115 tpd (13,71).

A variety of flue gas treatment processes for particulate and SO_x control are in the development and demonstration stages (37,38). Although the effectiveness of some of these processes is now being tested in fossil-fuel-fired utility boilers, their use for char-fed boilers has not been evaluated. It is reasonable to assume that these systems could be adapted to provide the necessary control for the char-burning processes. The adapted system would have to be environmentally sound (i.e. adequate control of all air, water, and solid waste streams) and efficient. Alternatively, development of a high-temperature char gasification approach may prove viable.

The emission of other gaseous pollutants from the char combustion operation, including CO and NO_x, are not now considered to present particular technical problems. Reported work with utility boilers (39) would indicate that careful control of the combustion process may suffice to produce acceptable levels in flue gas.

Adequate control of particulate emissions should result from the limestone scrubbing facility. Normal design practices would limit liquid droplet carry-over, would reheat gas downstream of the scrubber using hot-flue-gas exchange to prevent condensation and formation of visible plumes, and would insure that gas could not by-pass the scrubber in the reheat equipment by maintenance of an appropriate pressure balance. Use of hot flue gas to dry coal, as has been proposed in Section 2.1 above, would reduce the quantity of water required to presaturate the gas prior to scrubbing.

3.3.2 Cooling Water

A total of 260,000 gpm of cooling water is indicated to be required for operating the Bureau of Mines design. About two-thirds of this requirement is used for thermal exchange against the main high-pressure gasification train, so that considerable mechanical design effort is foreseen to minimize leakage losses into the cooling water system, which may otherwise preclude use of cooling towers as heat rejection devices. Undue leakage of hydrocarbons, CO, NH₃, phenols, H₂S, or sulfurous materials into the cooling water circuit could not be tolerated in the plumes from cooling towers. An early warning system to indicate the presence of hydrocarbons in cooling water return laterals will probably be required in any case to avoid noxious discharges.

If cooling towers were used for this total plant, a minimum of 6600 gpm of water would be evaporated. Drift loss would be in excess of 500 gpm, and draw-off might be about 800 gpm. Air requirement would amount to some 48,000 MM scfd. Reheat of plumes would be required to avoid fogs in some cases.

The design basis (10) includes only minimum heat integration, consistent with a conservative approach to an unproven design. Moreover, some 30 percent of the total cooling water requirement indicated for dust removal could be materially reduced if alternative procedures can be applied (See Section 2.4 above).

It is probable that environmental considerations and the costs of water reclamation will operate to restrict industrial water consumption in most domestic locations. Hence a commercial gasification design might maximize use of air-cooled heat exchangers, reserving the use of cold water only for "trim-cooling" or low-level heat transfer applications.

The overall economic balance will consider added investments in heat-exchange and electrical hardware associated with air-fin usage, as well as investment in incremental electrical generation capacity. Running costs for the generation of power and for equipment operation would be balanced against the net reduction in water treatment and pumping costs, as well as the net reduction in water loss.

On the basis that the indicated cooling water requirement for dust removal is eliminated, and that half of the remaining requirement may be displaced with forced draft air-cooled heat exchangers, the incremental electrical power requirement is estimated to amount to 24,000 KW. Added cooling water requirement associated with the incremental power generation would bring the net total cooling water requirement to an estimated 100,000 gpm, so that water loss by evaporation might be reduced to about 2600 gpm at the cooling towers. Drift loss would amount to 300 gpm on this basis. Blow-down, or draw-off from the system, might be held to 500 gpm. There would be a reduction in the steam usage indicated for pumping cooling water, such that the net incremental steam requirement for power generation might amount to 200,000 pounds per hour of 1000 psia steam, or to an equivalent thermal efficiency debit of about 1.5 percent.

The physical environmental situation at a particular site, including water availability, climatic conditions, and available area, will set limits on the designer's options for heat rejection. Other means, such as cooling ponds, may be practicable. In very special situations, it may prove economic to recover some of the low-level heat, as by circulation in central heating systems to nearby communities or in trade-off situations with irrigation water supplies, where hot water may be used to extend growing seasons. In all situations, the sociological impact of the use of the environment will be an over-riding factor.

3.3.3 Waste Water Treatment

Facilities required to treat water, including raw water, boiler feed water, and aqueous effluents, will include separate collection facilities:

- Effluent or chemical sewer
- Oily water sewer
- Oily storm sewer
- Clean storm sewer
- Cooling tower blowdown
- Boiler blowdown
- Sanitary waste

Retention ponds for run-offs and for flow equalization within the system will be required. Run-off from the paved process area could easily exceed 15,000 gpm during rainstorms. Run-off from the unpaved process and storage areas could exceed 60,000 gpm in a maximum one-hour period.

Pretreatment facilities will include sour water stripping for chemical effluents and Imhoff tanks or septic tanks and drainage fields for sanitary waste.

Gravity settling facilities for oily wastes will include API separators, skim ponds, or parallel plate separators.

Secondary treatment for oily and chemical wastes will include dissolved air flotation units, granular-media filtration, or chemical flocculation units.

Oxygen demand reduction may be accomplished in activated sludge units, trickling filters, natural or aerated lagoons, or by activated carbon treatment.

Boiler feedwater treatment will in general involve use of ion-exchange resins. Reverse osmosis, electrodialysis, and ozonation may find special application.

We consider that the Synthane plant will be able to take advantage of the properties of char and of attractive incremental costs for oxygen to assist its waste water treatment. Hence, the char produced by the process should have the attributes of activated carbon, which has been shown to be effective in the removal of a wide variety of the water contaminants expected (65). The Bureau of Mines design basis includes the use of forty-two tons per day of gasifier char for water treatment (48). Normally, the cost of activated carbon tends to restrict its use. If contaminated char so used may subsequently be fired in the utility boiler, water treatment in the Synthane system will be considerably simplified.

Similarly, oxidation of contaminants in water using oxygen, and especially ozone, is normally reserved for polishing drinking water supplies because of high costs. Direct oxidation, however, is very effective in reducing phenol, cyanide and thiocyanate levels in waste water (64), and has particular advantage in that solids concentrations are not thereby increased. We, therefore, believe that early research should be directed to the use of char and of oxygen or ozone to treat aqueous scrubber effluents from the Synthane process to set the stage for an integrated commercial design.

Evaporation will of course occur throughout this system, and the concern of the designers will be to limit the co-evolution of noxious or undesirable components which may be present. Of particular concern is the system which will be used to pretreat gas scrubber effluent (See Section 4.4). We note that it may be necessary to cover portions of the water-treatment facility and/or provide forced draft over some units to avoid undue discharge of hydrocarbons into the atmosphere. In the latter case, as with direct oxidation or ozonation, sweep gases would be ducted to an incinerator or boiler, and provisions for minimizing explosive hazard would be required.

3.3.4 Miscellaneous Facilities

Provisions for start-up of the gasification facility may generate short-term effluents to the atmosphere. Effluents from start-up heaters will depend on the fuel fired for such purpose. Product gas combustion in a boiler and/or in gas turbines may be justified to produce start-up steam and power requirements. In such case, reverse flow from the gas product delivery line may be practicable for fuel supply, or a pressurized gas storage facility might be provided on-site.

Planned noise reduction, especially in coal handling, grinding, and charging operations, hopper venting, and in the operation of large compressors and pumps, will be a requirement. Similarly, we note that normal commercial practice for high-pressure reaction vessels, and especially for oxygen-blown reactors, would provide barricade shielding or blast protection to limit damage in event of rupture and to protect personnel. Lay-out of the commercial Synthane gasification train will require sophisticated analysis to minimize the amount and cost of such shielding.

Operation of a blow-down system and flare stack to which accidental or emergency process releases may be directed will normally produce a small emission to the atmosphere.

4. LIQUIDS AND SOLIDS EFFLUENTS

Solid and liquid effluents based on our design are also shown in Figure 2 and Table 1.

4.1 Coal Preparation

On-site coal storage will require that facilities for containing storm run-off be provided. Hence, run-off from the 20-25 acre area required to hold a thirty-day supply of feed coal could easily amount to 5000 gpm during a major precipitation event common to almost all sections of the United States. Such run-off may be expected to contain acidic particulate matter from most contemplated feed coals.

It is assumed minimally that effluent limitation guidelines published by EPA for the coal mining industry under The Refuse Act Permit Program (41) will apply to such coal storage facility. The application of 'best practicable control technology' would require installation of impounding and settling facilities to be of sufficient size to handle run-off resulting from a once-in-ten-years' storm, and the operator would provide suitable recording analytical equipment, including a recording rain gauge, to guarantee compliance with concentration schedules for discharges into waterways.

Since permissible concentration schedules are such that impounded water will, after treatment, be of sufficient purity to be admitted to the plant's water system, it will be advantageous to plan for such use in the initial design. Similarly, run-off from the gasification complex otherwise will have to be contained. More than one set of water treatment facilities will be required to handle the various water streams coming from and going to the gasification plant. Depending on the severity of contamination that may be expected from the various processing areas, storm run-off from such areas would be directed to segregated holding facilities consistent with the expected water quality (See Section 3.3.3). It may be necessary to provide an impermeable subsurface barrier under certain portions of the facility, as the coal storage area, to prevent contamination of ground water.

Although not necessarily considered a part of the gasification facility, the coal mining operation, if it be located adjacent to the gasification complex, would probably share treatment facilities provided for the plant proper. Hence, typical acid mine drainage, of perhaps 300-400 gpm (42), might be treated continuously by accepted techniques (43, 44, 45), to produce water suitable for discharge or for plant use. Except for a separate initial holding pond and small lime addition facility, all other components of the treatment facility would amount to incremental increases on facilities which must be provided the parent plant.

If coal laundering is practiced, facilities for retention and disposition of liquid and solid effluents become more complex. Combinations of screening and thickening devices will generate streams of varying solids content, some of which would be considered refuse, and have to be returned to the mine or be buried otherwise. A properly designed system would minimize make-up water requirement by internal treatment and recirculation of wash water. A facility to launder feed coal for this design might circulate 2200 gpm of wash water, and discharge 1800 gpm along with thickened refuse. Such refuse would be impounded in clarifying basins, where evaporative loss would occur. Make-up requirements would then be held to such evaporative loss and to an estimated 500-600 gpm lost via the laundered coal product.

4.2 Coal Grinding

In this design, which incorporates bag filters on the air stream which issues from the ball mills, there should be no solid effluent from the coal grinding operation. Some 60 tpd of coal fines recovered at the filters is recycled to mill product.

4.3 Gasification

There should be no major solid or liquid discharges from the gasification section excepting the gasifier char stream. In our design, it has been assumed that a dry char let-down system can be developed, such that char may be ducted to the power plant using steam or inert gas as the transport medium. Char is generated at the rate of 4350 tpd.

Facilities used to store and compress lock hopper vent gas may generate small solids and liquid effluent streams that would require treatment or disposition. Hence, coal fines filtered from such vent gas are recycled to feed. Similarly, water present in such gas may be condensed in a compression process, and would be directed to treatment facilities. Water which may be used as sealing fluid in gas holders may likewise require periodic treatment and replacement.

4.4 Dust Removal

The "dust removal" or gas cleaning section as envisioned for this design has the greatest potential for pollution. It is at this point that all materials generated in the gasification (other than acid gas) that are not compatible with the gas product are removed. In Synthane gasification, as with all processes which gasify coal at intermediate temperatures, the gasifier output may contain all of the

products commonly associated with pyrolysis, carbonization, and coking of coals in addition to oxygenated products associated with partial combustion. Hence a broad spectrum of heavier materials present may be classified as tar, including phenols and cresols, pyridines, anilines, dihydric phenols (catechols), intermediate and high-boiling aromatics (naphthalenes), saturates, olefins, and thiophenes. Another grouping may be termed light oil and/or naphtha, including B-T-X, naphthalene, thiophene and condensable hydrocarbons and carbon disulfide. Ammonia will be present, and hydrogen cyanide, as well as coal, char, and ash fines.

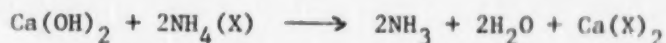
The particular distribution of compounds which will be present in raw gasifier gas will of course depend on the composition of feed coal and on the particular conditions of the gasification. The range of sulfur and B-T-X components which may be expected are listed in Table 3 for two types of coal (47).

In the design basis, cyclones and water-scrubbing are provided to remove condensable matter. Tars which may separate from such condensate have been partially characterized (Table 4). Similarly, aqueous condensate (obtained by passage of gasifier output from the Bruceton 40-atmosphere laboratory gasifier through water-cooled condensers) from Synthane raw gas has been analyzed, and compared with coke-plant weak ammonia liquor (Table 5).

We note that some of the polynuclear hydrocarbons which may be present in raw gas have exhibited carcinogenic properties in animal studies (67,68). Control of such materials will generally be required in connection with evaporation from the waste water treatment system, in plumes from cooling towers if leakage from the process train occurs, in the direct handling of separated tar or oil products, and in the flue gases from char, coal, or tar combustion (69,70).

The over-riding consideration is that gas clean-up shall be consistent with satisfactory operation of subsequent processing steps, especially shift conversion and methanation, and that Benfield solution contamination be minimized.

Scrubber operation for this design has been described in Section 2.4. The Bureau of Mines has evaluated the operation of facilities which may be required to treat waste water from this design (48). Aqueous effluent from the scrubber water decanters is fed to ammonia stills at the rate of 1,110,000 pounds per hour. Milk of lime is used to spring fixed ammonia in a steam-stripped tower according to



Generated lime sludge is directed to holding ponds for settling at the rate of 230 tpd (50% solids). CO_2 , H_2S , and HCN present in the incoming decanter stream are sprung in a heated dissociator. This gas stream is directed to the sulfur recovery unit. 160 tpd of ammonia is produced for sale. This general treatment method and its variations have been reviewed by Kohl and Reisenfeld (66).

Table 3
COMPONENTS IN GASIFIER GAS (47)
(ppm)

	<u>Pittsburgh</u> <u>Seam Coal</u>	<u>Illinois</u> <u>No. 6 Coal</u>
H ₂ S	860	9,800
COS	11	150
Thiophene	42	31
Methyl Thiophene	7	10
Dimethyl Thiophene	6	10
Benzene	1,050	340
Toluene	185	94
C ₈ Aromatics	27	24
SO ₂	10	10
CS ₂	--	10
Methyl Mercaptan	8	60

Table 4

MASS SPECTROMETRIC ANALYSES OF
BENZENE-SOLUBLE TAR
FROM SYNTHANE GASIFICATION (47)

Structural type; includes alkyl derivates	(Vol. %)	
	HP-118 ^{a/} #118 <u>Pittsburg</u>	HP-1 ^{a/} #92 <u>Illinois</u>
Benzenes	1.9	2.1
Indenes	6.1 ^{b/}	8.6 ^{b/}
Indanes	2.1	1.9
Naphthalenes	16.5	11.6
Fluorenes	10.7	9.6
Acenaphthenes	15.8	13.5
3-ring aromatics	14.8	13.8
Phenylnaphthalenes	7.6	9.8
4-ring peri-condensed	7.6	7.2
4-ring cata-condensed	4.1	4.0
Phenols	3.0	2.8
Naphthols	b/	b/
Indanols	0.7	0.9
Acenaphthenols	2.0	--
Phenanthrols	--	2.7
Dibenzofurans	4.7	6.3
Dibenzothiophenes	2.4	3.5
Benzonaphthothiophenes	--	1.7
N-heterocyclics ^{c/}	(8.8)	(10.8)
Average mol. wt.	202	212

^{a/} Spectra indicate traces of 5-ring aromatics.

^{b/} Includes any naphthol present (not resolved in these spectra).

^{c/} Data on N-free basis since isotope corrections were estimated.

Table 5

BY-PRODUCT WATER ANALYSIS^{1/} FROM SYNTHANE GAS (47)

	<u>Pittsburgh Seam</u>	<u>Illinois No. 6</u>	<u>Coke Plant</u>
pH	9.3	8.6	9
Suspended Solids	23	600	50
Phenol	1,700	2,600	2,000
COD	19,000	15,000	7,000
Thiocyanate	188	152	1,000
Cyanide	0.6	0.6	100
NH ₃	11,000	8,100 ^{2/}	5,000
Chloride		500 ^{3/}	
Carbonate		6,000 ^{3/}	
Bicarbonate		11,000 ^{3/}	
Total S		1,400 ^{4/}	

1/ Mg/liter (except pH)

2/ 85% free NH₃

3/ Not from same analysis

4/ S⁼ 400

SO₃⁼ 300

SO₄⁼ 1,400

S₂O₃⁼ = 1,000

Water withdrawn from the fixed ammonia still is cooled to 100°F using air-fin exchangers, and is stored for 48 hours to permit tars to separate. This water is then directed to aeration tanks, along with other aqueous streams condensed from the main product stream (see below). Antifoam, phosphoric acid, and sulfuric acid are added to adjust pH and to promote the oxidation of organic material, including phenols, cyanides, and thiocyanates, in the aerators.

Water from the aerators is directed to clarifying basins. Overflow, containing 0.2 ppm phenol, flows to polishing towers where gasifier char is used to remove phenols. Treated water is returned to the plant's raw water supply system at the rate of 1,760,000 pounds per hour. Wet char (about 1.75 tph of dry char is required) is re-directed to the gasifier char stream after filtration. Underflow from the clarifiers is filtered to remove sludge and recycled to the aeration tanks. Sludge is filtered and combined with char fuel going to the power plant at the rate of about 2.3 tpd. Filtrates are recycled to the aeration tanks.

One concern with this processing sequence involves the ultimate disposition of phenols. Particular difficulty associated with the recovery of dihydric phenols from aqueous streams led to the development in Europe of the so-called "Phenosolvan" process (49). In this scheme, n- or isobutyl acetate (or other acetate) is used as extraction solvent, permitting separation of phenol by-product.

It is interesting in this context to review the gas liquor treatment scheme provided for the Burnham Coal Gasification Complex (50). In this arrangement, incoming gas liquor is filtered and mixed with the Phenosolvan solvent. Phenol-rich extract is distilled to recover crude phenols, and the solvent overhead, after separation from water, is recycled to the extractors.

Crude phenol is used to scrub fuel gas, which is used to strip solvent traces from the extractor raffinate. Solvent-free raffinate is steam-stripped to remove NH_3 , CO_2 , and H_2S . The CO_2 and H_2S are returned to the sulfur recovery unit. Effluent from the strippers is directed to biological treatment to render it suitable for use as cooling tower make-up.

In recent years, the rapid development of environmental protection requirements has outstripped environmental research and development programs. It is likely that noxious effluent limitations will tighten in the future, so that considerable additional research is needed to offset the very high incremental costs foreseen for extended application of current technology. On the other hand, considerable progress has already been made toward practical treatment systems conforming with current standards in related coking and coal operations (40).

4.5 Shift Conversion

There should normally be no liquid or solid effluents from the shift operation. However, facilities will be required to dispose of spent or inactive catalyst (See Section 4.12).

4.6 Waste Heat Recovery

Some 395,000 pounds per hour of condensate is generated in the process of cooling combined gas streams prior to acid gas removal. Condensate is further cooled, and is then directed to the aeration tanks in the waste water treatment plant.

The depressurization of this, and all other condensates collected from the high-pressure gas stream, will release absorbed gas. It will be advantageous to direct all such condensates to a common expansion vessel, from which released gas may be recompressed back into the main gas stream. In particular, gases recovered from condensates ahead of methanation might be reinjected ahead of acid gas removal.

4.7 Gas Purification

Condensate streams are generated in the Benfield loop as circulated gas is cooled. The disposition of these streams will depend on their composition, but they may in general be directed to the waste water treatment plant. Some 19,000 pounds per hour of condensate is separated from treated gas as this stream is cooled ahead of the residual sulfur clean-up beds.

Additionally, facilities will be required to dispose of contaminated Benfield solutions. (See Section 4.12).

4.8 Residual Sulfur Cleanup

As previously discussed, facilities will be required to dispose of spent material used in the cleanup beds. Activated char or carbon may be combusted in the power plant, but disposition of other materials, such as iron oxide, is less certain (See Section 4.11.5)

4.9 Methanation

About 130,000 pounds per hour of condensate is separated from the main gas stream as it cools on exit from the methanation loop. Gas which separates from such condensate on depressurization may be compressed back into gas product, or may be consumed as fuel in the power plant. Condensate is directed to waste water treatment.

As discussed above, on-site facilities for catalyst replacement and activation may generate a variety of liquid and solid streams, including spent catalyst, metal dusts, and caustic solutions. Disposition of these materials is discussed in Section 4.12.

4.10 Gas Compression

A small quantity of condensate, about 1,000 pounds per hour, is separated from product gas in the final compression. Gas which separates on depressurization of this stream may be combined with gas evolved from methanation loop condensate.

4.11 Auxiliary Facilities

4.11.1 Oxygen Plant

About 85 gpm of water will be condensed from entering air at the oxygen facility. This water should be suitable for addition to the plant's boiler feedwater treatment system.

There should normally be no other liquid or solid effluents generated in the oxygen plant. However, if a refrigerant, such as ammonia, is employed in the refrigeration loop, facilities for disposition of such material will be required at intervals.

4.11.2 Sulfur Plant

Elemental sulfur make is about 140 tpd from the Stretford plant. Sulfur purity may be quite high, and product may be made available in solid or molten form, so that marketability should be high.

Sulfur recovery systems based on sodium, as in the Stretford system, require that the rhodanic salt resulting from the capture of cyanogen in the absorbent liquor, and thiosulfate and sulfate salts

resulting from oxidative side reactions, be continuously removed, and fresh alkali supplemented, to maintain recovery efficiency. The waste liquor withdrawn is very high in chemical oxygen demand, and is generally incinerated. The COD of this waste stream may be lowered by adding enough sodium to change the whole sulfur content to sodium sulfate prior to incineration. However, caustic requirement for this facility might amount to about a ton per hour.

An incineration process (51) has been developed to incinerate such waste liquor with a gas fuel under reducing conditions, such that sodium salts are decomposed to carbonates which may be captured and returned to the Stretford system. This process results in zero liquid or solid effluent, but is high in energy cost and investment.

4.11.3 Power and Steam Generation

The largest solid effluent stream from the boiler will be ash. Ash in the coal feed to the gasifiers amounts to about 1050 tpd. Most of this material is removed from the gasification train with char and, if char is burned as fuel in the power plant, this same ash will be discharged at the boiler. There will be small ash "losses" to tar, and ash will otherwise appear in raw gas and in scrubbing liquors and condensates.

The quantity of ash discharged from the boiler will of course depend on the degree of efficiency with which the fuel (char) is combusted. Hence, a carbon combustion efficiency of 96 percent would increase the ash rate about 10 percent above theoretical. Similarly, it is not now known what the composition of such ash may be otherwise, especially with regard to sulfur content and to particular toxic trace elements which may affect the costs for ultimate disposition of this material. It is now considered that ash effluents would be buried in a mine in a manner that would minimize subsequent adverse environmental impact.

If limestone is used to treat flue gas to limit SO₂ emissions, about 150 tpd of sulfated lime will be generated. Long-term disposition of such material is likewise uncertain. It may ultimately be required that sulfur be recovered, as by regeneration of the sulfated material.

4.11.4 Cooling Water

A variety of chemical additives may be used to treat water circulated in the cooling system to control algae and corrosion. These will appear in tower draw-offs, along with matter originally present in make-up streams. Depending on the extent of facilities provided to treat waste water effluents, such draw-offs may be treated

to precipitate or neutralize specific toxic elements, such as chromium or zinc, before being directed to further treatment.

As indicated above, there may be particular problems associated with leakage into the cooling water system from the high-pressure gas processing train. In general, however, such leakage would be expected to add to atmospheric emissions at the cooling towers, with only trace quantities of condensable liquids or solids appearing in the cooling water circuit.

4.11.5 Miscellaneous Facilities

A variety of materials is indicated to be required to treat waste water effluents, including milk of lime, antifoam, phosphoric and sulfuric acids, and char or activated carbon. In addition, water treatment may require the use of lime-soda alums, ion exchange resins, caustic, ferrous ion, and chlorine, among other agents. Ultimately, these additives exit the system as concentrated sludges, contaminated solids, or in aqueous streams with high salt content. These effluents may be concentrated, dried, and/or incinerated. Ultimate disposition of the dry or concentrated residuals is uncertain, however, especially if heavy metals, leachable salts, or organic contaminants are present. Burial in sealed pits appears the only practicable method for disposal of materials which must be prevented from leaching into ground or surface water, although the logistics and economics of such techniques requires extensive further study.

4.12 Maintenance

Normal plant operations will require the periodic replacement or replenishment of catalysts and other chemical agents used to process coal and gas. Such maintenance will generate contaminated solid and liquid effluents, including shift catalyst, Benfield solution, methanation catalyst, activated carbon, iron oxide, and caustic streams. In general, spent materials will be sulfidic. Metal value may justify specific reclamation, but again, it would appear that the ultimate disposition of such solid effluents is now uncertain. Incineration or thermal oxidation, as in a fluid bed incinerator, might be used to remove hydrocarbon and sulfur, but control of metallic particulates from such systems requires further study, as does the disposition of residues.

Operation of start-up heaters will generate solid or liquid effluents consistent with the fuel consumed. Hence, if coal is fired, ash and stack treatment effluents may be accumulated, and subsequently directed to the operating plant's normal treatment routing.

5. THERMAL EFFICIENCY

The efficiency with which energy is utilized ranges from less than 5 percent for the ordinary incandescent lamp to perhaps 75 percent for a well-maintained home heating furnace. The automobile engine has an efficiency of less than 20 percent. Modern fossil fuel power plants are not more than twice as efficient. On the average, probably less than 35 percent of the available heat in fuels consumed in the United States is recovered usefully (52).

The determination of thermal efficiency is useful for providing a basis on which to compare like processes, or to gauge incentives for process improvements. Obviously, there are other equally important bases on which processes may be compared, including economic and ecologic factors associated with process improvement or increases in efficiency. In large measure, such costs may be related to the technological state of an art. Hence, it is unlikely that more efficient methods for converting energy to visible light will find widespread use until a device that is as convenient, inexpensive, and reliable as the incandescent lamp is developed.

In the case of fossil fuel conversion processes, the thermal efficiency is calculated as the ratio of the heating value of product(s) to the heating value of the (coal) feed. In the present design, the higher heating value for coal feed, based on the analysis given for Pittsburgh seam coal as fired to the gasifiers (10), has been estimated by conventional formulas to be approximately 13,700 Btu per pound, which is at variance with the heating value reported. Product gas is indicated to have a higher heating value of 927 Btu per scf, a value consistent with its analysis. Similarly, a thermal credit of 130,000 Btu per gallon is taken for recovered tar, which is considered a saleable product. On this basis, a base thermal efficiency of 63.5 percent is indicated (See Table 6). Since tar is not a "clean" product, we note that its thermal value should be discounted in the event that it is not marketable as such.

The basis otherwise assumes that char may be completely combusted to balance the plant's steam and power requirements. If, for example, a carbon combustion efficiency of only 96 percent is achieved in the char combustion process, the shortfall would be equivalent to about one percent on feed coal, so that overall efficiency would drop about the same amount. We have assumed that a carbon combustion efficiency of 100 percent will be achieved.

The design basis (10) does not include specific allowance for treatment of scrubber effluent. The Bureau of Mines design (48) for waste water treatment, including scrubber effluent, requires the energy equivalent of 2.6 percent of gasifier feed coal for its operation, in addition to an

incremental 24,000 gph of raw water which must be upgraded to boiler feedwater. If this energy requirement were to be generated by burning coal or tar along with char in the powerplant, so that additional desulfurization of flue gases or its equivalent would be required, overall process efficiency would be reduced about four percent below baseline. However, credit might then be taken for the heating value of separated ammonia, amounting to about 0.8 percent of feed coal equivalent.

Although recovered tar should be valued higher than feed coal for the purpose of supplying the volatile component that may be required to achieve stable char combustion, such tar would be combusted if it could not be marketed. Combustion of all of the tar would balance the utility load estimated for waste water treatment.

As discussed in Section 2.7, the base design does not include distinct facilities for separation of oils, naphtha, or phenols. It has been estimated that about 25,000 gpd of B-T-X may be produced (47), in addition to 60,000 gpd of tar oil and 15,000 gpd of crude phenol in a plant of this size, although it must be emphasized that the exact quantities of these materials which may be extractable from gasifier output will be distinct functions of the composition of feed coal and of the particular conditions of the gasification. We estimate the thermal efficiency debit associated with the removal of hydrocarbon, including crude distillation, will be about equal to the thermal credit for the separated material.

The design basis does not include specific provision for drying feed coal. If moisture content of feed coal had to be reduced an incremental five percent due to moisture accumulation on storage, the thermal requirement amounts to about 0.5 percent of the feed coal. We believe that flue gas from the utility boiler may be used to effect such drying, avoiding this energy debit (See Section 2.1).

Similarly, substitution of a Stretford sulfur recovery system for a direct oxidation Claus plant will significantly increase utility requirements associated with sulfur recovery, but the effect on overall efficiency is minor, on the order of 0.2 percent.

As discussed in preceding sections, there are numerous opportunities in the proposed system which a designer may consider for energy recovery or energy reduction. In all such cases, the potential energy benefit must be weighed against the costs associated with such recovery, including not only investment, but also factors associated with operability, increased processing complexity or decreased overall reliability, and potential hazards. In many cases, the technology is not straightforward, so that additional research and development will be required. Obvious areas for such investigation include the methods for feeding coal to the gasifiers and for extracting char, and the potentials for energy recovery in the dust removal and gas purification systems as proposed.

We have estimated that more than 300,000 pounds per hour of high-pressure steam may be generated if a tar scrubber can be applied to gasifier output (Section 2.4). Further, 300,000 pounds per hour of low-pressure steam may be additionally generated in subsequent water scrubbing/cooling of raw gas, simultaneously reducing cooling water load and the associated energy debit.

Similarly, we have estimated that 100,000 pounds per hour of high-pressure steam may be generated in the char let-down process, or that the bulk of the sensible heat of char may be conserved if a dry char let-down process is developed.

If air-fin cooling is substituted for cold water exchange as outlined in Section 3.3.2, the net energy debit is estimated at about 1.5 percent, but net water loss in the cooling water circuit can be reduced by more than half.

Finally compression energy required to deliver final product gas to commercial pipelines is conserved in the Synthane system by operation of the gasification train at essentially pipeline pressure. It may be desirable to consider operation of the system at some reduced pressure. Hence, operation at the 600 psi level would bring much of the required hardware within the realm of commercial experience and safety codes, such that development lead times and potential process hazards may be considerably reduced. The final gas compression debit in this case should amount to no more than about one percent on overall efficiency. Such consideration, of course, must also weigh factors related to the effect of pressure on gasifier output and to required reaction volumes. Additional development will be required before this effect can be properly assessed.

Table 6
THERMAL EFFICIENCY

	Quantity	Equivalent MMBTU/Hr	Thermal Efficiency as Percent of Gasifier Feed
<u>Bureau of Mines Synthane Design Basis (10):</u>			
Coal*to Gasifiers (TPH)	593.75	16,270	--
Product Gas (MSCFH)	10.41	9,650	59.3
Tar (GPH)	4849.	630	3.9
Sulfur (TPH)	5.7	45	0.3
			<u>63.5</u>
<u>Bureau of Mines Water Treatment Base Case (48)</u>			
- Equivalent Coal Feed (TPH)	15.24	420	-2.6
			<u>60.9</u>
<u>Estimated Effects of Additions and Modifications</u>			
- Incremental Flue-Gas Treatment, Sludge Dewatering and Handling, Boiler Feedwater Treatment, Ash Handling Associated with Power and Steam Generation for Waste Water Treatment.			
+ Produced Ammonia (TPH)	6.6	220	-1.3
- Hydrocarbon Removal and Distillation		130	+0.8
			<u>60.4</u>
+ Produced Hydrocarbon (GPH)	1000	115	-0.7
		130	+0.8
			<u>60.5</u>
- Stretford Sulfur Recovery Substitution For Claus Plant		35	-0.2
			<u>60.3</u>
- Product Gas Loss in Acid Gas Removal		50	-0.3
			<u>60.0</u>
+ Steam Generation in Tar Scrubber		540	+3.3
+ Steam Generation in Water Scrubber and Credit for Cooling Water Reduction, Less Energy Associated with Scrubber Operation and Steam Production.		300	+1.8
+ Steam Generation in Char Let-Down		150	+0.9
			<u>66.0</u>
- Air-Fin Substitution for Cooling Water		250	-1.5

6. SULFUR BALANCE

The sulfur balance for this design (see Table 7) has been estimated using a variety of sources (11,33,47) along with the design basis (10). The analytical results reported by the Bureau of Mines for various laboratory gasification experiments for Pittsburgh seam coal are not necessarily mutually consistent with the design basis. However, the estimate is reasonable if reported values for organic sulfur levels in raw gas are assumed (47).

Approximately 60 percent of the sulfur in the gasifier coal feed appears as H_2S in the gasifier output (10). Essentially all of the sulfur in this form, including that portion dissolved in aqueous condensates, may be recovered as saleable elemental sulfur product. Depending on relative economics, the concentration of H_2S in the CO_2 stream separated at the sulfur plant may be reduced to less than 5 ppm, so that it may be practicable to dispose of this stream by passing it up the stacks of the main boilers.

Nearly 30 percent of the incoming sulfur is retained in the gasifier char in this case. It is probably not reasonable to expect that all of this sulfur will be oxidized in the char combustion process. We have arbitrarily assumed 96 percent conversion to SO_2 (equivalent to about 0.25 percent sulfur in final ash). The flue gas scrubber on the char boiler will be required to remove at least 6100 pounds per hour of SO_2 , so that less than 4800 pounds per hour may issue to the atmosphere in the scrubbed flue-gas stream. If limestone is used in the scrubbing system, some 12,300 pounds per hour of sulfated lime will be generated at theoretical conversion. In practice, the quantity of limestone required and the amount of solid residual produced may be half again as much (13,71).

Concentrations of organic sulfur compounds in raw gas reported for Synthane gasification of Pittsburgh seam coal (47) appear quite low, especially with regard to carbonyl sulfide. However, it may be assumed that COS and mercaptans present in gas subjected to catalytic shift conversion will be hydrolyzed to H_2S and CO_2 , so that organic sulfur will be thereby reduced by half (in the shift by-pass stream). Moreover, depending on the scrubbing procedures used to treat raw gas before shift conversion, or to extract naphtha or oil components from the gas stream, more or less of the organic sulfur compounds may be diverted to other streams.

Research relating to the Benfield acid gas removal process (74) indicates that COS removal in commercial systems ranges from 75 to 99 percent, mercaptan removal ranges from 68 to 100 percent, and disulfide removal ranges from 71 to 85 percent. And 85 percent removal of thiophene has been reported for a commercial installation, although this effect runs counter to expectation or to laboratory test results. In general, most of such absorbed sulfur would

appear as H_2S in regenerator off-gas. Undesirable reaction products (sulfates, thiosulfates, thiocyanates, polysulfides) appear to accumulate in the activated hot carbonate solution only to a limited and acceptable extent. Hence it would appear that organic sulfur levels would be reduced by at least 70 percent on average in the Benfield system. Such compounds which persist beyond this point would be removed in the sulfur guard beds preceding methanation.

Sulfur which is present in aqueous condensates collected from the gas processing train will undergo varying treatment in the waste water treating plant depending on the overall quality of the particular stream. H_2S which separates on depressurization of such streams, or which issues from the ammonia recovery system, will be directed (along with CO_2) to the sulfur recovery plant. Although it is not possible to designate how much sulfur may be sprung to atmosphere in aeration/oxidation facilities which may be provided for water treatment, very close control of such emissions will be required. Hence, the bulk of dissolved sulfur will issue generally in calcium sludges or in chars (activated carbon) from the treatment plant. These accumulated residuals would be de-watered and fed to the main char boilers for incineration.

The concentration of sulfur in tar separated from the gas stream is estimated, on the foregoing basis, at about 2.5 percent. This is higher, by a factor of three, than the results obtained in a reported laboratory gasification (47). However, the distribution of sulfur among the various component sub-streams issuing from the gasifier has been shown to be primarily a function of coal feed composition and of gasification conditions, and may be further influenced by the manner in which the streams are separated.

Table 7

SULFUR BALANCE

	<u>Lb/Hr</u>	<u>Percent</u>
In Feed Coal	19,000	
H ₂ S Converted to Sulfur Product	11,400	60.0
Char From Gasifier	5,435	28.6
[Final Ash	210	1.1
As SO ₂ in Flue Gas	2,290	12.1
As Sulfated Residual from Flue-Gas Scrubber	2,935	15.4
Organic Sulfur in Raw Gas*	165	0.9
(Thiophene, Mercaptan, Sulfides)		
[Hydrolyzed in Shift Converter	80	0.4
Hydrolyzed in Benfield	55	0.3
Sulfur Guard	30	0.2
Total Sulfur in Aqueous Condensate*	935	4.9
[Recovered as H ₂ S	270	1.4
Oxidized/Released to Atmosphere	100	0.5
As Sludge to Incineration	565	3.0
Tar (By Difference)	1,065	5.6
		<u>100.0</u>

* Estimated per Reference 47.

7. TRACE ELEMENTS

Trace elements are usually defined as those elements present to the extent of 0.1% (1000 ppm) or less. Nearly all trace elements show an enrichment in coal ash relative to their crustal abundance (53). Manganese and volatile elements such as mercury are exceptions. This enrichment is attributed to concentration effects or exchange reactions during the formation of coals. Almost every element has thus been found in coals, but the variation in concentrations is quite broad (12).

The fate of trace elements present in the feed coal to conversion processes has so far received little attention. To the extent that such conversion processes approach conditions which obtain during combustion, it may be pertinent to apply results obtained in trace element studies of the combustion of coals (54,55,56). Even in such studies, however, the conditions of combustion have been noted to affect element dispositions. Coal handling and preparation methods can likewise influence results, so that generalizations may not be meaningful. Obviously, extrapolation to a particular conversion process or feed coal would be conjectural in large measure.

Although very large quantities of coal are consumed in combustion processes, so that the total quantities of trace materials, some of which are highly toxic, that may be released are likewise large, it has been only recently that concerted effort has been directed to the definition of the real problems. This effort, of course, has been associated with the promulgation of sanctions affecting permissible discharges to the atmosphere and waterways of the United States. Particular sanctions relating to toxic discharges are still in process of formulation (57). Research is required in many cases not only to set limits and goals, but also to develop analytical procedures that may be generally adapted. With fossil fuels, the general problem relates to the complexity of the chemical system, including the large number of components, the imprecision of available sensors or test methods, and the difficulties associated with representative sampling of very large streams. The detection and monitoring of many trace elements requires sophisticated procedures and equipment which cannot be practically applied commercially. In fact, the magnitude and nature of many industrial streams is such that direct quantification or measurement is impractical. The general nature of the pollution problem associated with Synthane gasification has been described by the Supply-Technical Advisory Task Force (58). At this point it is generally considered that gasification will present no insurmountable control problems. On the other hand, it is seen that considerable research will be required to establish practical and economical control procedures.

Trace elements which have been detected by the Bureau of Mines in condensate from the laboratory Synthane gasifier are shown in Table 8 for an Illinois No. 6 coal (47). Similarly, toxic trace elements which have been found in Synthane raw gas and tar are shown in Table 9.

Literature values (12) for the elemental composition of Pittsburgh seam coals are presented in Tables 10 through 12. Reported values may of course not be representative of a particular coal; but in many cases, element levels are remarkably consistent in a particular region.

Table 10 lists the major elements in coal (exclusive of C,H,O,N). On the basis that reported values may apply to the feed coal in the present design, we have calculated the quantity of each element which daily enters the process via the gasifiers. Similarly, for the purpose of comparison, we have calculated the quantity of each of these elements which would appear in the condensate from raw gas if reported values (47) were to apply to the present design. Obviously, we would expect the bulk of these materials (other than sulfur) to exit the process via the ash residual from char combustion. But the elements vary widely in the form in which they appear in coal and in their reactivity, volatility, and solubility otherwise.

Table 11 similarly lists some of the minor or trace elements in feed coal. It should be emphasized that concentrations of some of these elements can vary by factors of ten or more within a region, and that analytical methods employed by researchers have had high or unmeasured inherent imprecision in many cases. Reported values may also suffer from bias in some cases, in that analyses were performed on coals which were known to contain high concentrations of particular elements; and the original intent of the analyst has not always survived reprinting of his data.

HCN, mercury, and arsenic have been detected in raw gas and in tar from Synthane gasification by the Bureau of Mines (47). These materials are listed in Table 12, a tabulation of some of the hazardous trace elements in coal prepared on the same basis as the preceding tables. For these elements especially, it will be important to close the material balance. Recently reported studies indicate the difficulty associated with the attempt to follow mercury, for example, throughout a commercial coal-fired utility installation. But the state-of-the-art of detection is bound to progress rapidly as attention is focused on particular elements through legal sanctions, and as coal processes proliferate.

Each developer of a coal conversion process may ultimately be required to account for the disposition of elements present in feed whose toxicity or ultimate impact on the environment warrants control. He may moreover be required to guarantee the containment or neutralization of such materials in effluent streams, and this, in turn, may influence the adoption of particular processing alternatives, even including the conditions of gasification. For Synthane, this will require additional research firstly to define the levels of these elements through the

Table 8

TRACE ELEMENTS IN CONDENSATE FROM AN
ILLINOIS NO. 6 COAL-GASIFICATION TEST (47)

	<u>No. 1</u>	<u>No. 2</u>	<u>Average (by wt)</u>
Ca	4.4	3.6	4 ppm
Fe	2.6	2.9	3 ppm
Mg	1.5	1.8	2 ppm
Al	0.8	0.7	0.8 ppm
Se	401	323	360 ppb
K	117	204	160 ppb
Ba	109	155	130 ppb
P	82	92	90 ppb
Zn	44	83	60 ppb
Mn	36	38	40 ppb
Ge	32	61	40 ppb
As	44	28	30 ppb
Ni	23	34	30 ppb
Sr	33	24	30 ppb
Sn	25	26	20 ppb
Cu	16	20	20 ppb
Nb	7	5	6 ppb
Cr	4	8	6 ppb
V	4	2	3 ppb
Co	1	2	2 ppb

Table 9

TRACE COMPONENTS IN RAW GAS* AND TAR (47)

COAL FEED	RAW GAS		TAR	
	HCN ppb by vol.	Hg ppm by vol.	Hg ppm by wt.	As ppm by wt.
Ill. Char	5	-	-	-
Ill. #6 Coal	20	0.00001	0.003	0.7
W. Kentucky	11	-	-	-
N. Dak. Lignite	3	-	-	-
Wyoming Sub-Bit.	2	-	-	-

* It is indicated that no mercury or HCN was detected in product gas.

Table 10

MAJOR ELEMENTS IN COAL

	<u>Concentration in Feed Coal (Wt. %)</u>	<u>In Feed to Gasifier lb/day</u>	<u>Concentration in Condensate (47) (ppm)</u>	<u>Discharge to Water Treatment lb/day</u>
Si	4.0	1,140,000	--	--
Fe	1.5	428,000	3	50
S	1.6	456,000	1400	22,500
Al	1.0	285,000	0.8	13
Ca	0.5	142,500	4	65
K	0.22	62,700	0.16	3
Mg	0.17	48,500	2	32
Na	0.069	19,700	--	--

Table 11

MINOR TRACE ELEMENTS

	<u>In Feed</u>		<u>In</u>	
	<u>Coal</u>		<u>Condensate</u>	
	<u>ppm</u>	<u>lb/day</u>	<u>ppm (47)</u>	<u>lb/day</u>
B	165	4700	--	--
Ba	100	2900	0.13	.2
Zn	44	1250	0.06	1
V	35	1000	0.003	0.05
Li	25	710	--	--
Cr	22	620	0.006	0.1
Ni	14	400	0.03	0.5
Ge	12	340	0.04	0.6
Cu	12	340	0.02	0.3
Mn	10	290	0.04	0.6
Mo	8.2	230	--	--
Y	7.7	220	--	--
La	5.1	150	--	--
U	5	140	--	--
Co	3.8	110	0.002	0.03
Sn	1.5	43	0.02	0.3

Table 12

POTENTIALLY HAZARDOUS TRACE ELEMENTS

	<u>In Feed Coal (ppm)</u>	<u>To Gasifier lb/day</u>		<u>(PPM)</u>	
			<u>Condensate</u>	<u>Raw Gas*</u>	<u>Tar</u>
Be	2	60	-	-	-
F	85	2430	-	-	-
As	31	880	.03 (.5)**	-	0.7 (.7)
Se	2.2	65	.36 (6)	-	-
Cd	0.14	4	-	-	-
Hg	0.2	6		*** .0001 (.04)	.003 (.003)
Pb	7.7	220	-	-	-
HCN	-	-	-	*** 20 (1000)	-

* No Hg or HCN detected in product gas.

** Numbers in parentheses indicate quantities in pounds per day appearing in design streams.

*** Units as given in Reference (28).

process sequence for particular feed coals at preferred gasification conditions. A preliminary study of this type has been reported for the Hygas bench-scale unit (59). Additional research may then be required to indicate specific modification of the process sequence to remove or contain these materials or to adequately plan effluent treatment facilities.

It would appear, on the basis of results published thus far, that Synthane gasification does not appear to introduce new control problems. Rather, since the gasification train and water loops, including run-off, may be designed to be largely self-contained, emphasis of the controls development will be directed to flue gases and ash from the combustion process that powers the system, to the gas residual from acid gas treatment, and to the concentrated residuals from waste water treatment. The enormous current government/industry effort to define and set effluent goals and to develop economical control procedures for coal-fired industrial operations will have a direct bearing on the extent of additional research that may be required, once stream compositions have been completely defined for Synthane gasification.

8. PROCESS ALTERNATIVES

Most of the process alternatives which we have considered in connection with the particular design chosen as the basis for this report will require additional research, development, and/or evaluation. Some would change or diffuse the character of the process. Operation of the process at a lower pressure, for example, would influence all aspects of the design and each such aspect would have to be evaluated for its effect on the total design, including investment and costs. On the other hand, most of the laboratory results published thus far relating to this process have been obtained at pressures considerably below the 1000 psi level, so that extrapolation to high pressure has already introduced a measure of uncertainty. The primary process considerations which may be affected by pressure include gasification rates, raw gas composition, dust removal operations, and acid gas removal. In fact, there are so many such inter-related considerations which may affect the overall efficiency, cost and pollution potential, that it is not particularly useful to extend analysis in the absence of real data. Operation of a prototype plant over a range of pressures should ultimately resolve this question.

Similarly, the use of a high temperature gasification process to gasify char and tar separated from the Synthane train to produce a clean fuel for power generation, and so avoid flue-gas desulfurization, appears now to be viable processing alternative. On the other hand, there is bound to be further development of desulfurization processes, and a continuing redefinition of applicable standards, as well as development of combustion processes for chars and tars, so that constraints which face the ultimate designer may be substantially different from those that now appear.

Other processing alternatives which suggest themselves include:

- Use of a tar scrubber as a first element in the dust removal operation. Incentives include reduction in water treatment loads and thermal efficiency credits.
- Alternative facilities for adjusting gas composition ahead of methanation, including the possibility of auxiliary coal gasification for this purpose. Gasification of char and/or tar to produce a hydrogen-rich gas may also be attractive.

- Use of extraction processes to remove phenols, for example, from scrubber effluent.

Even if particular alternatives are evaluated at a given stage in a process's development and found to be marginal, it may be necessary to re-evaluate these same options at a later stage as basic data are firmed. Hence, the development of alternatives continues, even through the life of a commercial plant.

Table 13 lists some of the alternatives considered in connection with the base design.

Table 13

PROCESS ALTERNATIVES CONSIDERED

Coal Drying

- Coal-fired vs use of boiler flue gas.
- Lime-scrubber vs electrostatic precipitator or bag filters.
- Flash drying in ball mills.

Gasification

- Variations on lock-hopper coal charging operations.
- Char let-down process variations.
- Operation at lower total pressure.

Dust Removal

- Inclusion of tar scrubber and internal gasifier cyclones vs external cyclones and water scrubbing.
- Inclusion of facilities to remove middle and light oils from product gas.

Shift Conversion

- Alternative means for adjusting gas composition ahead of methanation.
- Improvements in shift conversion processes.

Acid Gas Treatment

- Use of Stretford process vs Claus plant and tail-gas cleanup.
- Inclusion of facilities to convert organic sulfur to H₂S and to treat Stretford blow-down.

Utilities

- Alternative fuel choices for power and steam generation.
- Waste-water treatment variations, including use of process char and oxygen or ozone. Use of extraction for phenol removal.
- Maximum air-fin usage vs cooling water for heat rejection.

9. ENGINEERING MODIFICATIONS

Engineering modifications that may be advantageous will occur to the detail designer. Obviously, these cannot be divorced from process considerations, but rather will reflect an attempt to optimize energy utilization or reduce investment or operating cost within process constraints.

As discussed above, operation of this process at high pressure on a commercial scale will involve development of hardware that is currently non-existent. While reaction volumes are small, wall thicknesses are large and stresses are high, so that vessel costs and operating hazards may not be optimum. The engineering, design, and operation of this system will be considerably simplified if operating pressures are substantially reduced, based on current technology. On the other hand, this is not seen to imply that technology should not be extended, or that engineering considerations should prevail over processing benefits that may be seen for operation at high pressure.

A number of engineering alternatives involve integration of facilities. The net increase in thermal or material efficiency that may result must be balanced, in general, against increased process complexity and/or costs or reduced operating reliability. Hence, the use of hot flue gas from the utility boiler to dry feed coal has been incorporated into our design. On the other hand, this alternative constrains the relative placement of the coal drying and boiler facilities, and the start-up and operation of these facilities is made more complex, involving inter-related controls.

Similarly, attempts to minimize energy requirements for compressing lock-hopper gas that depend on the scheduling of gasifier operations must be assessed on the basis of potential for decreased overall reliability or the slowing of overall operation.

The location of a given facility within the total plant may be optimized on the basis of one or more major considerations, but will in general prove non-optimum from other viewpoints. Hence the air intakes for the oxygen facility might be located to minimize interference from plant effluents. But it will also be desired to minimize piping and hardware required to deliver oxygen to the gasifiers.

Incentives for other modifications will depend on future process development. There would now appear to be considerable incentive for energy recovery on depressurization of scrubber effluent. This processing sequence will almost certainly be improved in the course of future research.

A major modification that deserves attention, as with most preliminary gasification designs, is the general substitution of air fin cooling for the use of cooling water. This may prove especially important in this case, since the high operating pressure increases the possibility of leakage into the cooling water system and subsequent emission at the cooling towers. Again, basic economics and the designer's ingenuity will dictate whether, and to what degree, such substitution may be practicable.

Table 14 lists some of the engineering modifications considered in connection with the base design.

Table 14

ENGINEERING MODIFICATIONS CONSIDERED

Coal Drier

- Use of limestone scrubber to treat boiler flue gas drying medium.

Gasification Train

- Operation at lower pressure.
- Treatment of depressurized gases and condensates.

Dust Removal

- Power generation on depressurization of scrubber effluents.
- Steam generation in cooling raw gas.

Acid Gas Removal

- Power generation on depressurization of scrubber effluent.

Methanation

- Provision for limiting CO in product gas.

Utilities

- Air-fin substitution for cooling water.
- Containment of run-off and inclusion in plant water balance.

10. QUALIFICATIONS

This study is based on the process design (Figure 1 and Tables 15-17), supplied by the process developer (10,48), with modifications as discussed and shown in Figure 2 and Table 1. Costs or economics were not considered, except directionally. Although it was not always possible to resolve process details with assigned energy or mass consumptions, overall assignments are considered reasonable and consistent with the data obtained at the laboratory level (8,11,22).

Variations in feed coal and product compositions make it difficult to compare gasification processes. Significant variation is seen even for the "same" process on different coals. Similar variation will extend to the pollution potential of the process. Considerable additional research and/or development will be required to define pollutant levels in particular streams with the precision required by today's standards, and so permit a more accurate assignment of energy requirements.

Table 15

COAL AND PRODUCT ANALYSES

Pittsburgh Seam

Coal Feed to Gasifier (10)

	<u>Wt. Per Cent</u>
C	73.8
H ₂	5.2
N ₂	1.5
S ₂	1.6
O ₂	8.0
Ash	7.4
Moisture	2.5
HHV	13,700 Btu/lb.

Product Gas to Pipeline

	<u>Mol Per Cent</u>
H ₂	3.6
CO	0.1
CO ₂	3.7
CH ₄	90.4
N ₂	2.1
H ₂ O	0.1
HHV	927 Btu/scf

Table 16

PLANT UTILITY REQUIREMENTS (10)

Unit	Steam Production and Consumption, Pounds Per Hour						Electric power, kw/hr/hr	Cooling water, gpm	Raw makeup water, gpm
	1,000 psia @ 800°F Consumed	1000 psia @ saturation Produced	1000 psia @ saturation Consumed	50 psig @ saturation Produced	50 psig @ saturation Consumed				
Coal preparation	135,000						1,810	4,610	
Gasification	93,200						140	5,900	2,410
Dust removal	78,200							77,160	
Shift conversion	548,900								
Waste heat recovery									
Purification							35		1,100
Methanation	5,700		258,600				40	72,420	95
Pipeline compression	8,100	506,800					1,000	9,710	1,475
Oxygen plant	601,800							520	105
Sulfur recovery								60,070	
Subtotal	1,470,900	506,800	1,487,800	809,600	737,600	20	20	230,410	20
Steam plant ¹		1,300,000	64,800				3,045		5,205
Powerplant								4,450	570
Utilities:									
a. cooling water									
b. plant lighting			103,400					5,670	9,100
c. sanitary water									
General facilities							800		
Miscellaneous and contingencies	69,100		150,800		72,000		600		1,000
Total	1,540,000	1,806,800	1,806,800	809,600	809,600		400	19,470	500
							1,155		1,625
							6,000	260,000	18,000

(1) Steam plant produces 1,540,000 pounds per hour of 1,000 psia, 800°F steam in addition to saturated steam.

Table 17

COAL AND PRODUCT QUANTITIES AND HEAT CONTENT

Coal Consumption

	<u>TPH</u>	<u>Equiv. MM BTU/Hr</u>
Coal to Gasifiers (10)	593.75	16,270
Equivalent Coal to Utility Boiler for Water Treatment (48)	<u>15.24</u>	<u>420</u>
	609.0	16,690

Products and Equivalents

Product Gas (MM SCFH)	10.41	9,650
Tar (gph)	4849	630
Sulfur (tph)	5.7	45
NH ₃ (tph)	6.6	130
B-T-X (gph)	1000	<u>130</u>
		10,590

11. RESEARCH AND DEVELOPMENT NEEDS

The Bureau of Mines, as developers of the Synthane Process, have, with The Lummus Company, designed a versatile pilot plant now under construction, which is geared to the determination of many of the basic data which will be required to design a commercial plant. The following paragraphs discuss research and development needs that bear on the efficiency and/or pollution potential of the process.

Paramount among the research needs will be demonstration of the operability of the integrated gasification system. Hence the following operations must be demonstrated simultaneously in a continuous manner:

- Coal Feeding, involving lock hopper operation
- Coal Pretreatment, involving fluidized bed operation
- Gasification, involving fluidized bed operation
- Char Let-Down, involving continuous withdrawal from a fluidized zone and lock hopper operation

Achievement of operability in the prototype pilot plant will almost certainly involve developmental modifications.

Equally important will be the determination of basic gasification parameters on gas composition and gasification rates, including the effects of:

- Feed Coal Properties/ Pretreatment
- Total Pressure
- Temperature
- Steam/ Oxygen Ratios
- Carbon Conversion

Perhaps the most important aspect of this program will be the data which may be used by the designer of the commercial gasification system to optimize gasifier total pressure. Investment and operating costs for each component of the total system, including auxiliary facilities, will be affected by the gasification pressure level, as will the overall thermal efficiency and pollution potential of the process. Detailed parametric analysis based on data to be obtained at Bruceton should point the way to an optimum design.

The third major objective of the pilot plant program involves the ultimate selection for development of one of the two novel Bureau of Mines methanation processes, Tube Wall Reactor (TWR) or Hot

Gas Recycle (HGR), both of which have been included in the prototype unit. This selection will evolve from operations on a much larger scale than heretofore, and over a broader total pressure range. These results may significantly affect process thermal efficiency.

Obviously, initial effort in the pilot plant program will be heavily weighted toward achievement of primary goals. It was considered that such achievement must precede secondary developments that may be required to commercialize the process. Included among such developments are:

- Development of a char-burning boiler
- Optimization of "dust removal" from raw gas

There is indicated to be no facility provided in the prototype plant for char combustion studies. From some points of view, this may be considered a serious deficiency. However, there are a number of coal conversion processes undergoing development which produce similar chars, so that progress in char conversion and combustion may be otherwise expected. Moreover, as has been already discussed, unless significant progress is shown for flue gas desulfurization, it may prove more attractive to gasify char, bypassing combustion development entirely. It will of course remain to be demonstrated that Synthane char may be gasified, but this is now considered to be a low-risk option.

The problem of raw gas treatment, on the other hand, is not nearly so straightforward. There will be processing constraints on the quality of gas that may be admitted to shift conversion and subsequent gas treating operations, as these processes are now visualized. Hence reliable operation of the catalytic shift converter and of the Benfield acid gas removal process, both of which have been included in the prototype plant, may prove the best yardstick for judging the efficacy of dust removal.

Apart from processing constraints, the method of raw gas treatment may have significant impact on overall efficiency and on the pollution potential of the process. Hence the degree to which gas must be cooled to effect clean-up and the particular procedures employed will translate to energy and water requirements and, specifically, to the quantities of "contaminated" streams that must be further processed for economic or ecologic reasons. The prototype plant has been provided a flexible gas scrubbing system which should point the way to a practicable design. We have also suggested a variation on this design, incorporating a tar scrubber as the leading element in the dust removal operation. This device has been commercially proven for petroleum fluidized bed coking operations, but at generally less severe operating conditions than will be required here. We see considerable incentive for the development of this or some similar technique, however, which avoids or reduces the thermal and pollution debits of the aqueous scrubber.

It is unfortunate that it is not possible a priori to specify the exact quantities and nature of materials which will have to be removed from raw gas. These will depend as much on the conditions of gasification as on the properties of the particular feed coal. It is similarly not possible to pre-judge how variation in pretreatment or gasification parameters may affect such residuals. Hence the approach taken in the pilot plant program, which will firstly optimize the gasification on the basis of primary yields, appears to be a logical choice. Moreover, successful operation of the pilot plant will mean that particular requirements for at least one practicable system will have been established.

It is presumed therefore that future or secondary developments will:

- Optimize raw gas treatment on the basis of overall thermal efficiency. Research efforts may be directed to "hot gas" clean-up, to improved shift conversion catalysts or procedures, or to alternative means for adjusting hydrogen content before methanation.
- Optimize raw gas treatment on the basis of pollution potential. Obviously, these developments cannot be divorced from each other, or from the primary requirement to deliver a clean product gas. Research may be directed to procedures for neutralizing or recovering materials from "contaminated" streams generated in the clean-up process, or to operations on the main gas stream. Specific problems may include the dephenolization of aqueous scrubber streams, or the removal of HCN, thiophenes, or COS from the main gas stream or from the acid gas separated by the Benfield system.

The pilot plant will also permit evaluation of the Benfield acid gas removal process over a broader pressure range than heretofore. A better definition of the kinds of treatment that may be required for both the main product stream and for the acid gas that is separated should evolve. Moreover, the inclusion of a Stretford scrubber in the prototype plant should serve to flag any unwanted interactions between the acid gas removal and sulfur recovery processes, again establishing the basis for a practicable commercial design.

On the basis that successful operation of the pilot plant will be achieved, it will thereafter be possible to investigate any aspect of the process to any desired degree of precision. On the other hand, in the current domestic energy framework, a decision to commercialize may be required before all research or optimization studies can be completed. It may be important finally only to know that the process is workable, that efficiency is reasonable, and that adverse environmental impact is within reasonable tolerances. The questions relating to environmental impact may be the most difficult to resolve quickly.

The concentrations of residuals in processing streams that may bear on environmental impact can be very low. Even at the greatly expanded prototype plant scale (relative to previous laboratory-scale), it may not be practicable to resolve all possible problems. It is considered that:

- Special effort should be made in connection with the earliest operations of the prototype pilot plant to instrument or to otherwise provide for analysis of trace components known to be toxic or undesirable. Routine analytical methods for many trace elements and compounds are not available, and must be developed. In many cases, sophisticated laboratory procedures only may be applicable, and precision is poor. Commercial plant magnitudes will be 200-300 times greater than the prototype plant scale, so that judgements relating to commercial design could easily be misdirected.
- The varying composition of coal, and the difficulties associated with representative sampling of solid streams, makes it extremely difficult to obtain balances for trace elements around coal operations. The multiphase nature of the output streams from many coal conversion processes or treatments adds to the general problem. And representative sampling becomes more difficult for any stream as the stream size increases.

The proper interpretation of prototype pilot plant results will be greatly simplified if clear balances are shown around processing equipment. Sampling systems should be designed to permit such balances to be generated with a high degree of confidence. Special effort should be directed to sulfur in all its forms, HCN, arsenic, mercury, cadmium, and metal carbonyls.

- Because the Synthane process generates char which exhibit many of the desirable properties of activated carbon and because incremental oxygen should be available from the Synthane oxygen plant at relatively low cost, we consider that early research directed to the use of these materials for treatment of Synthane effluents may lead to greatly simplified pollution control systems for water and gas loops. Hence research may be directed to the use of char in fixed- or fluidized-bed units to treat gas streams, including the main product stream (65), or to treat liquid effluents, especially waste water streams, for the removal of specific constituents. In general, the use of char for pollution control would be viable only if it could be demonstrated that flue gases from the subsequent combustion of contaminated

char were compatible with standards for atmospheric discharges, or could readily be treated to make them so. It would not, for example be particularly useful to take COS from one stream and discharge it to the atmosphere in another. Hence additional research, which should be coupled with the char combustion development, would be required to demonstrate overall effectiveness.

Similarly, the use of oxygen or of ozone, especially for the oxidation of contaminants in waste water, warrants attention. Direct oxidation using these materials is advantageous in many cases because residuals which form when other oxidants such as chlorine are used are avoided. Moreover, oxidative reactions which go slowly or not at all with air frequently go rapidly with ozone or oxygen, so that the sizes of treating facilities and treat times are reduced. Such oxidation does introduce questions relating to corrosion, toxicity, explosive hazard and relative costs, all of which factors may be inherent in any treatment method, but which can be assessed in the research program.

- Finally, there is a growing need to conduct research related to toxic or noxious materials that is not specific to Synthane gasification, but which relates to all fossil-fuel utilization. Obviously, toxic elements which enter a process must concentrate or exit the process at some point. Not only are the quantities discharged important, but so also must be the form in which such discharged materials appear. There is hardly any form or compound of mercury, for example, which may not be considered toxic or hazardous in some sense. But there are obviously relative degrees of toxicity associated with its various compounds, and work is required to define these least toxic forms, as well as to develop technology for conversion to desired forms within the process framework. A more realistic approach to control of some elements or compounds which cannot be effectively concentrated or extracted from effluent streams may be their conversion to the least objectionable forms in such streams.

Zero direct discharge to atmosphere or to waterways may be technologically possible within the gasification process battery limits, but the desired objectives will not be achieved if discharged ash, concentrated sludges, or solid streams contaminate the environment at some later time. The magnitude of this problem is very great, but so also is the combined effort which may be brought to bear by affected industries, consumers, and regulatory agencies to achieve a solution.

12. BIBLIOGRAPHY

- (1) Forney, A. J., R. F. Kenny, S. J. Gasior, and J. H. Field, "Destruction of Caking Properties of Coal by Pretreatment in a Fluidized Bed", Ind. Eng. Chem. Prod. Res. Develop., Vol. 3, No. 1, March, 1964, pp. 48-53.
- (2) Forney, A. J., R. F. Kenny, S. J. Gasior, and J. H. Field, "The Production of Nonagglomerating Char from Caking Coal in a Continuous Fluid-Bed Reactor", Preprint-Division of Fuel Chemistry, American Chemical Society, Vol. 8, No. 3, Aug.-Sept., 1964, pp. 1-9.
- (3) Gasior, S. J., A. J. Forney, and J. H. Field, Ind. Eng. Chem. Prod. Res. Develop., Vol. 3, 1964.
- (4) Forney, A. J., R. F. Kenney, S. J. Gasior, and J. H. Field, "Fluid Bed Gasification of Pretreated Pittsburgh Seam Coals", Advances in Chemistry, Am. Chem. Soc., Vol. 69, 1967, pp. 128-140.
- (5) Forney, A. J., S. J. Gasior, R. F. Kenny, and W. P. Haynes, "Steam-Oxygen Gasification of Various U.S. Coals", Second Int. Fluid-Bed Combustion Conf., Hueston Woods State Park, Ohio, Oct. 1970.
- (6) Forney, A. J., R. J. Demski, D. Bienstock, and J. H. Field, "Recent Catalyst Developments in the Hot-Gas-Recycle Process", BuMines R.I. 6609, 1965.
- (7) Haynes, W. P., J. J. Elliott, A. J. Youngblood and A. J. Forney, "Operation of a Sprayed Raney Nickel Tube-Wall Reactor for Production of a High-BTU Gas", Preprint - Div. of Fuel Chemistry Symposium, A.C.S., Vol. 14, No. 4, Sept., 1970, pp. 26-48
- (8) "Engineering Evaluation and Study of the Bureau of Mines "Synthane" Process", The M. W. Kellogg Company, December 21, 1970.
- (9) Frith, J. F. S., "Engineering Aspects of the Synthane Coal Gasification Process", Second Synthetic Fuels from Coal Conference, Oklahoma State University, Stillwater, Oklahoma, May, 1972.
- (10) "An Economic Evaluation of the Synthane Gasification of Pittsburgh Seam Coal at 1000 psia", BuMines Report No. 72-9A, October, 1971.
- (11) Mills, G. A., "Progress in Coal Gasification - U.S. Bureau of Mines", Proc. Third Synthetic Pipeline Gas Symposium, Rosemont, Illinois, November, 1970, pp. 57-78.
- (12) Magee, E. M., H. J. Hall, and G. M. Varga, Jr., "Potential Pollutants in Fossil Fuels", EPA-R2-73-249, June, 1973.

- (13) Slack, A. V., H. L. Falkenberry, and R. E. Harrington, J. Air Pollution Control Assoc., Vol. 22, No. 3, March, 1972, p. 159-166.
- (14) Magee, E. M., Jahnig, C. E. and Shaw, H., "Evaluation of Pollution Control in Fossil Fuel Conversion Processes, Gasification, Section 1, Koppers-Totzek Process", EPA "NTIS PB No. 231 675/OWP".
- (15) Foster Wheeler Corporation, private communication.
- (16) Weir, H. M., "High Pressure Gasification of Coal in Germany", Ind. Eng. Chem., Vol. 39, 1947, pp. 48-54.
- (17) Forney, A. J., S. J. Gasior, W. P. Haynes, and S. Katell, "A Process to Make High-BTU Gas from Coal", Bu. of Mines Technical Progress Report 24, April, 1970.
- (18) Final Report, Coal to Gas Prototype Pilot Plant, U.S. Bureau of Mines, Contract No. HO 110989, The Lummus Co., October, 1972.
- (19) Cheng, C. Y., L. T. Fan, and J. A. Hunter, RGD Progress Report No. 357, Office of Saline Water, U.S. Dept. of the Interior.
- (20) Benson, H. E., J. H. Field, and R. M. Jameson, Chem. Eng. Prog. Vol. 50, No. 7, 1954, pp. 356.
- (21) Benson, H. E., J. H. Field, and W. P. Haynes, Chem. Eng. Prog. Vol. 52, No. 10, 1956, pp. 433.
- (22) Field, J. H., H. E. Benson, G. E. Johnson, J. S. Tosh, and A. J. Forney, "Pilot-Plant Studies of the Hot Carbonate Process for Removing Carbon Dioxide and Hydrogen Sulfide", Bureau of Mines Bulletin 597, 1962.
- (23) Ricketts, T. S., "The Operation of the Westfield Lurgi Plant", I.G.E. Journal, October, 1963, pp. 563.
- (24) Newman, L. L., "Oxygen in the Production of Hydrogen or Synthesis Gas", Ind. Eng. Chem., Vol. 40, No. 4, April, 1948, pp. 559-582.
- (25) Sands, A. E., H. W. Wainwright, and L. D. Schmidt, Ind. Eng. Chem., Vol. 40, 1948, pp. 607.
- (26) Sands, A. E., H. W. Wainwright, and G. C. Egleson, "Organic Sulfur in Synthesis Gas", Bureau of Mines Rept. of Investigations 4699, 1950.
- (27) Corey, R. C., "Bureau of Mines Synthane Process", Second Synthetic Fuels for Coal Conference, Oklahoma State University, May, 1972.

- (28) Forney, A. J., and J. P. McGee, "The Synthane Process - Research Results and Prototype Plant Design", Proc. Fourth Synthetic Pipeline Gas Symp., (Amer. Gas Assoc.), Chicago, 1972, pp. 53.
- (29) Hydrocarbon Processing, April, 1971, p. 119.
- (30) Ellwood, P., Chem. Eng. Vol. 71, No. 15, July 20, pp. 128-130 (1964).
- (31) British patent No. 1,049,918, Nov. 30, 1966.
- (32) British patent No. 1,154,482-3, July 11, 1969.
- (33) S. Katell, private communication.
- (34) McCann, C. R., J. R. Demeter, A. A. Orning, and D. Bienstock, "Combustion of Pulverized Char", Proc. 162nd Natl. ACS Meeting Div. of Fuel Chemistry, Vol. 15, No. 2, Sept., 1971, pp. 96-105.
- (35) Hammons, G. A., and A. Skopp, "A Regenerative Limestone Process for Fluidized Bed Coal Combustion and Desulfurization", EPA, Feb., 1971.
- (36) "Background Information for Proposed New-Source Performance Standards", U.S. E.P.A., PB 202 459, August, 1971
- (37) "Control of Air Pollution from Fossil Fuel-Fired Steam Generators Greater Than 250 MM BTU Per Hour Heat Input", EPA.
- (38) "Survey of Processes and Costs for SO_x Control on Steam-Electric Power Plants", NAPCA, Div. of Proc. Cont. Eng., August 24, 1970.
- (39) Crawford, A. R., E. H. Manny, W. Bartok, and R. E. Hall, "NO_x Emission Control for Coal-Fired Utility Boilers", Presented at AIChE 66th Annual Meeting, Philadelphia, November 11-15, 1973.
- (40) Kostenbader, P. D., and J. W. Flechsteiner, "Biological Oxidation of Coke Plant Weak Ammonia Liquor", Jrnl. Water Poll. Cont. Fed., Chicago, Ill., Sept. 1968.
- (41) "Coal Mining Industry - Effluent Limitation Guidance", EPA, September 5, 1972.
- (42) Calhoun, F. P., "Treatment of Mine Drainage with Limestone", Proc. Second Symp. on Coal Mine Drainage Research, Mellon Institute, Pittsburgh, Pa., May, 1968 pp. 386-391.
- (43) Mikok, E. A., M. Duel, C. E. Chamberlain, and J. G. Selmerzi, "Mine Water Research - The Limestone Neutralization Process", BuMines R.I. No. 7191, 1968.

- (44) Duel, M. and E. A. Mikok, "Mine Water Research - Neutralization" BuMines R.I. No. 6987, 1967.
- (45) Kim, A. G., "An Experimental Study of Ferrous Iron Oxidation in Acid Mine Water", Proc. Second Symp. on Coal Mine Drainage Research, Mellon Institute, Pittsburgh, Pa., May, 1968.
- (46) Matula, J. P., H. N. Weinberg, W. Weissman, "Flexicoking", presented at 37th Midyear Meeting of API Division of Refining, New York City, May 11, 1972.
- (47) Forney, A. J., W. P. Haynes, S. J. Gasior, G. E. Johnson, and J. P. Strakey, Jr., "Analyses of Tars, Chars, Gases, and Water Found in Effluents from the Synthane Process", Bu. Mines Application of Improved Technology to Provide Clean Energy Program, Tech. Prog. Report 76, January 1974.
- (48) "An Economic Evaluation of Waste Water Treatment for a 250 MM SCFD Synthane Plant", U.S. Dept. of the Interior, Bureau of Mines Report No. 73-22, April, 1973.
- (49) Rhodes, E. O., "German Low-Temperature Coal Tar Industry", Bureau of Mines I.C. 7490, February, 1949.
- (50) El Paso Natural Gas Company, Burnham Coal Gasification Complex, Stearns-Roger Incorporated, Denver, Colorado, August 16, 1972.
- (51) Mitachi, E., "Cleaning Na Absorbents in Tailgas Recovery Circuits," Chem. Eng., October 15, 1973, p. 78.
- (52) Rose, D. J., "Energy Policy in the U.S.", Scientific American, Vol. 230, No. 1, January, 1974. p. 20.
- (53) Abernethy, R. F., M. J. Peterson, F. H. Gibson, U. S. Bureau of Mines R.I. 7281 (1969).
- (54) Schultz, H., E. A. Hattman, and W. B. Booker, ACS Div. of Fuel Chem., Vol. 8, No. 4, p. 108, August, 1973.
- (55) Bolton, N. E., ACS Div. of Fuel Chem., Vol. 8, No. 4, p. 118, August 1973.
- (56) Billings, C. E., A. M. Sacco, W. R. Matson, R. M. Griffin, W. R. Coniglio, and R. A. Harley, "Mercury Balance on a Large Pulverized Coal-Fired Furnace", Jrnl. Air Poll. Cont. Assoc., Vol. 23, No. 9, Sept., 1973, p. 773.
- (57) Lee, R. E., et al, Journ. Air Poll. Control, 23, (10), October, 1973.
- (58) Synthetic Coal-Gas Task Force, National Gas Survey, Federal Power Commission, April, 1973.

- (59) Attari, A., EPA Report 650/2-73-004, August, 1973.
- (60) Knabel, S. J., and Tsaros, C. L., U.S. Dept. of Interior, Office of Coal Res. R&D Report No. 22, Interim Report No. 3, 1967.
- (61) Rudolph, P.F.H., "The Lurgi Process", presented at the 4th Synthetic Pipeline Gas Symposium, Chicago, October, 1972.
- (62) Busch, R. G., "Fluid Coking", Oil and Gas Journal, April 6, 1970, pp. 102-111.
- (63) Lowry, H. H., "Chemistry of Coal Utilization", Supplementary Volume, John Wiley, 1963, p. 587.
- (64) Chemical Week, November 3, 1971, pp. 53-55.
- (65) Wainwright, H. W., L. J. Kane, M. W. Wilson, C. C. Shale, and J. Ratway, IEC, Vol. 46, No. 7, July, 1956, pp. 1123-1133.
- (66) Kohl, A. L. and F. C. Riesenfeld, Chemical Engineering, Vol. 66, No. 12, June 15, 1959, pp. 127-178.
- (67) Hartwell, I. L., Public Health Service Publication No. 149, 1951.
- (68) Sarvicki, E. and K. Cassel, Nat'l. Cancer Inst. Monograph No. 9, 1962.
- (69) Hangebrauck, R., D. Von Lehmden, and J. Meeker, J. Air Pollution Control Assoc., Vol. 14, No. 7, July, 1964, pp. 267-278.
- (70) Cuffe, S. T. and R. W. Gerstle, Public Health Service Publication No. 999-AP-35, 1969.
- (71) Saleem, A., J. Air Pollution Control Assoc., Vol. 22, No. 3, March, 1972, p. 1973.
- (72) Mandelik, B. G. and C. V. Pierson, Chem. Eng. Prog., Vol. 64, No. 11, Nov., 1968, p. 75.
- (73) Chem. Eng., Vol. 75, May 6, 1968, p. 94.
- (74) Parrish, R. W. and Neilson, H. B., "Synthesis Gas Purification Including Removal of Trace Constituents", 167th National ACS Meeting, Div. of Industrial and Eng. Chemistry, Los Angeles, California, March 31, 1974.